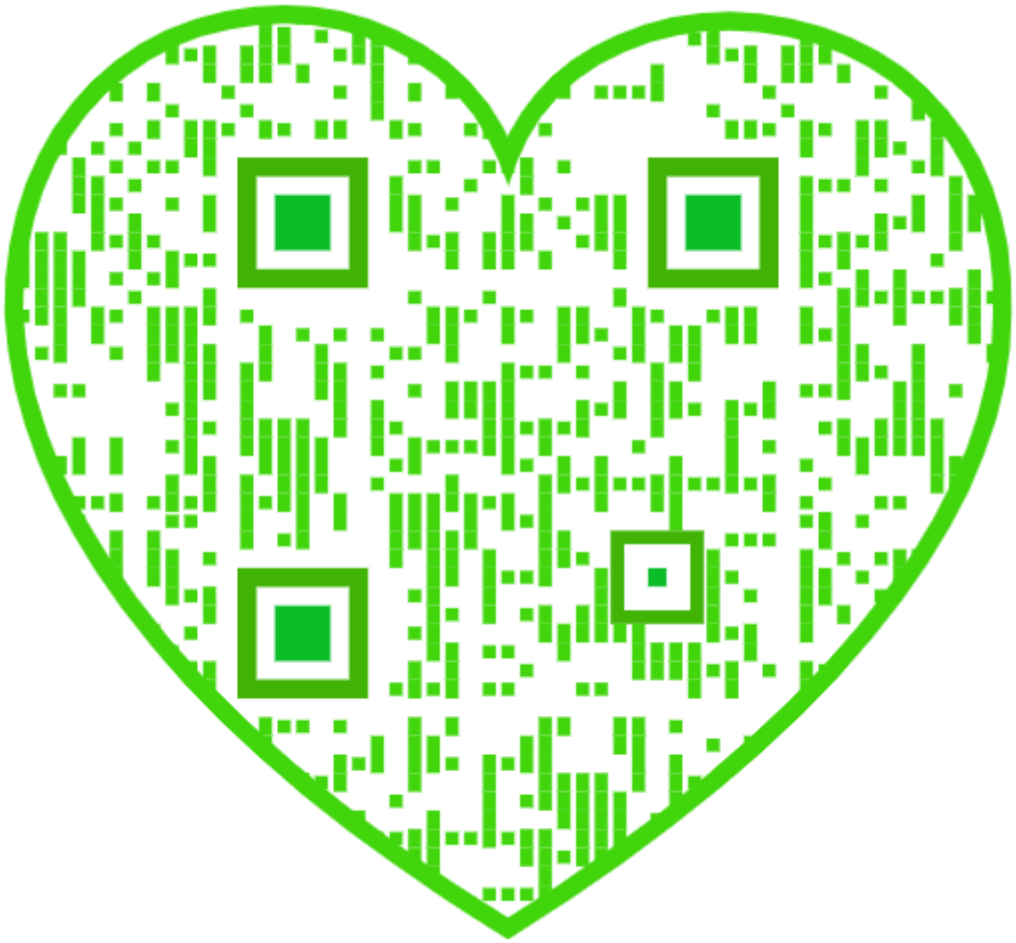
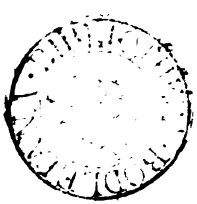


CHEMICAL PHENOMENA

OF

IRON SMELTING.

AN EXPERIMENTAL AND PRACTICAL EXAMINATION OF THE CIRCUMSTANCES WHICH DETERMINE THE CAPACITY OF THE BLAST FURNACE, THE TEMPERATURE OF THE AIR, AND THE PROPER CONDITION OF THE MATERIALS TO BE OPERATED UPON.



BY

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PREFACE.

THE first blast furnace erected with especial reference to smelting the ironstone now known as the Cleveland was built, under my own superintendence, in 1846, at the Walker Works, on the Tyne. The stone itself was brought from the neighbourhood of Whitby, and the furnace had a capacity of about 3,500 cubic feet.

A year or two afterwards, Messrs. Bolckow & Vaughan commenced to smelt the same ore in furnaces having a capacity of only 2,850 cubic feet, which they had built at Witton Park, in the hope of obtaining supplies of material from the immediate neighbourhood.

I mention these circumstances to show that at the periods in question, whatever had been done in the erection of larger furnaces elsewhere, the results had not been such as to induce my late friend, Mr. John Vaughan, or myself to venture on departing from dimensions of a very moderate character; indeed, in the course of our constant communication on the subject, I made known to him the fact, that at the Wylam furnace, containing only 2,350 cubic feet, we were doing work as efficiently as in that at Walker, nearly one half larger.

In the year 1850, ironstone, obtained from the Eston mines, was sent to Witton Park, and, in consequence of the favourable yield, three furnaces were erected in 1851 at Middlesbrough to smelt it. They were only 42 feet high, with a capacity of 4,566 cubic feet. These were followed the next year by two others, 45½ feet high, of 5,100 cubic feet capacity, the property of Messrs. Gilkes, Wilson, Pease and Co.

There was nothing in the consumption of fuel at any of these furnaces to indicate the existence of any advantage over the Wylam furnace of little more than half the size, for on referring to my early note books, 35 to 37 cwts. of coke were often consumed

to produce a ton of grey iron, and I have known it as high as two tons.

In the month of January, 1854, my partners and myself blew in, at the Clarence Works, what were at the time the three largest furnaces in the district, viz., 47½ feet high, having a capacity of 6,174 cubic feet. Up to thát period little had been done in applying the escaping gases as a means of heating the blast, Mr. Vaughan having discontinued its use from the trouble involved in cleaning the stove pipes.

Impressed with the importance of having the air highly heated, and independently of any attention on the part of the workmen, we made the use of the gases to the air stoves at the Clarence works the first object of study, and from the high temperature obtained, and its regularity, we speedily reduced the coke consumption considerably below 30 cwts. to the ton of iron.

The following list contains the other furnaces erected on the banks of the Tees up to the end of 1858*:—

				No. of furnaces.	Feet high.	Cubic feet.
1853.	Eston ...	Messrs.	Bolckow & Vaughan	6	54	7,116
1854.	Ormesby	„	Cochrane & Co. ...	4	55	7,175
„	South Bank	Mr.	Samuelson ...	3	50	5,050
„	Cleveland	Messrs.	Bolckow & Vaughan	3	54	7,116
„	Tees-side ...	„	Gilkes, Wilson, Pease, & Co.	2	55	6,800
1856.	Stockton	„	Holdsworth & Co. ...	3	50	6,341
„	Norton ...	„	Warner & Co. ...	3	50	6,000
1858.	Claylane ...	„	Elwon & Co., designed by Mr. Vaughan	3	56	7,000
„	Tees-side ...	„	Gilkes, Wilson, Pease & Co.	2	56½	7,200
„	Normanby	„	Jones & Dunning ...	3	58	8,000
„	Witton ...	„	Bolckow, Vaughan & Co.	1	61	7,950
„	Tees ...	„	Snowdon & Hopkins	2	55	7,700

* "Increase in Size of the Cleveland Furnaces," by J. Gjers.—"Journal of Iron and Steel Institute," Nov., 1871.

Having constant opportunities of ascertaining the duty performed by nearly the whole of the above named furnaces, in many cases from actual copies of their consumption sheets, I was so satisfied that no perceptible advantage had been derived from an increase of dimensions gained entirely by an addition to the height, that other three furnaces were erected at Clarence, subsequent to 1858, of the same size as those already mentioned, making the entire number, six.

In the year 1861, Messrs. Whitwell erected three furnaces at Thornaby, 60 feet high, but having boshes of 20 feet, their cubic capacity was 12,778 feet. Occasionally, I heard of very favourable results being obtained at this establishment, but nothing beyond those sometimes attending the use of the furnaces at the Clarence Works, which, in the year 1860, occasionally worked at 25 cwts., and, not unfrequently, at 26 to 27 cwts. for grey iron. It may be remarked that it is quite possible that, in the comparison which I have attempted, in this somewhat rough manner, to draw between furnaces up to a capacity of 6,000 cubic feet, due regard was, perhaps, in the absence of all authentic information, not paid to the more or less efficient way in which the blast they received was heated. Had this invariably been done, I dare say, differences in favour of the larger furnaces would have been perceived. That this is highly probable would appear from the fact, communicated to me by my friend, Mr. William Whitwell, from which it would appear, that when the blast was maintained at the Thornaby Works at 900°F. the consumption of coke over a whole year averaged about 25 cwts. to the ton of iron.

Such was the condition of things when the means of raising the temperature of the blast beyond anything conceived as possible, was proposed by Mr. E. N. Cowper, in his fire-brick stove, and its power in this respect was tried at the Clarence Works in 1861, and somewhat earlier than this by the Messrs. Cochrane, at Ormesby, in both cases on the furnaces already spoken of.

The next important step in the history of ameliorating the

process of smelting iron was the erection, late in 1862, at Middlesbrough, of a furnace designed by Mr. Vaughan. It was of smaller cubic capacity than that of Messrs. Whitwell, viz., 11,985 cubic feet, instead of 12,778, but it was 75 feet high, instead of 61.

Mr. Vaughan having reported to me an improvement in its performance compared with the old furnaces, I proceeded, by his permission, to endeavour to ascertain the causes of the difference, and to a certain extent these were communicated in a report to the British Association for the Advancement of Science in the following year.

I was so satisfied of the superiority of this change in the form, that I had plans prepared immediately for a pair of furnaces, 80 feet high, with a capacity of 15,500 cubic feet; and other firms acting in like manner, within eighteen months several new establishments were set to work, varying from 67 feet to 81 feet in height, and containing from 12,000 to 17,700 cubic feet.

The iron manufacturers of the district by this time had in these enlarged furnaces, blown with air, capable of melting zinc in four to six seconds, probably 850°F. to 900°F., reduced their consumption of coke to something like 22½ cwts. for the ton of iron, and the question which presented itself to their minds was,—supposing the absence of any mechanical difficulty, how far this enlargement of size could be profitably carried, *i.e.*, would a further increase of dimension be followed by a reduction in the consumption of fuel, or, would it merely enable a larger quantity of iron to be smelted in a given time?

In the absence of all systematic investigation of the real nature of the required conditions in smelting iron, before the end of 1868 furnaces were erected of enormous dimensions, the largest being those at Ferryhill, 103 feet high, and containing upwards of 33,000 cubic feet.

The first public attempt to examine the subject scientifically was made by Mr. Charles Cochrane, before the Society of Mechanical

Engineers, in November, 1868.* In the paper read before this body, it was pointed out that the actual quantity of coke necessary in a blast furnace was that demanded for the reduction and carburizing of the iron, which he estimated at 7·43 cwts. per ton of metal, and Mr. Cochrane himself having, in the meantime, had great experience with air, heated by means of Cowper's stoves, had applied it to furnaces having a capacity of 20,624 cubic feet. In the discussion which followed the reading of his communication, he expressed a hope, that by increasing still further the dimensions of the furnace, enough heat might be conveyed into the furnace with the blast to enable a ton of iron to be produced from Cleveland stone with 13 cwts. of coke.

At the same meeting, I communicated shortly the reasons which prevented my agreeing with the opinions expressed by Mr. Cochrane, and these were extended, in the same year, in a paper read before the members of the Iron and Steel Institute, entitled, "The Development of Heat, and its Appropriation in Blast Furnaces of Different Dimensions."

The information contained in this communication was chiefly that derived from observations made on the furnace itself, and then it was that I became aware how much there remained to be learnt of the laws which regulate the process of iron smelting, before any one could look into the future history of the operation with any degree of certainty. Under these circumstances, I commenced at once a very long series of experiments to determine, if possible, the nature of the reactions which take place among the substances dealt with in the manufacture of pig iron.

In the course of my previous labours, I felt how important it was that I should have an opportunity of studying the behaviour of furnaces, working under a variety of conditions, before arriving at any general conclusions on the enquiry I had proposed to myself. The opportunity of doing this could only be obtained by the co-

* *Vide* their Proceedings, January, 1869.

operation of other manufacturers, and this was afforded in so unreserved a manner, that I felt, the least return I could make to those who had assisted me, was the free communication of opinions, their services had assisted me in forming. To carry out this design, in a series of papers which appeared in the JOURNAL of the Iron and Steel Institute, I have made known a great number of the experiments and observations undertaken in connection with the object I had in view, and as these, possibly, may have an interest to others besides the members of that body, they are here presented in a separate form.

WASHINGTON, COUNTY DURHAM,
15th February, 1872.

CHEMICAL

PHENOMENA OF IRON SMELTING.

SECTION I.—INTRODUCTION.

My occupation as a pig iron manufacturer, extending over more than twenty-five years, has afforded me many opportunities of studying the practical results produced at the blast furnace. More recently mere observation of the process of smelting has been supplemented by experimental research, the first fruits of which were communicated, by desire of the Chemical Society, in a paper to be found in their Transactions for May, 1869. Since that period more extensive investigation has somewhat modified the opinions expressed in the communication to that body, and has added to the information previously possessed. To some extent, my views in respect to the consumption of fuel in iron-smelting, as affected by the size of the blast furnace and the temperature of the air, have been submitted to the criticism of the members of the Society of Mechanical Engineers, and of the Iron and Steel Institute, and the results may be found in the Proceedings of these two associations. In the meantime, the performance of a number of furnaces of different constructions, and using different materials, has been carefully studied on the spot, a task which I have been able to perform by permission, most readily granted, of esteemed colleagues in the iron trade. The experience thus obtained opened out an extensive field of enquiry for the chemical laboratory, involving the performance of many experiments requiring great delicacy of manipulation. To assist me in these, I have had the advantage of the coöperation of Mr. C. R. A. Wright, D.Sc., who has bestowed the greatest care in carrying out my wishes in connection with a somewhat prolonged and laborious investigation.

For upwards of forty years the nature of the chemical changes which take place during the reduction of ores of iron, and the union of the resulting metal with carbon, have engaged the attention of scientific men.

It is the combination of these two actions which constitutes the manufacture of pig iron; and it is easy to understand that a process involving the study of the three elements, iron, carbon, and oxygen, should possess peculiar interest for the chemical philosopher.

To the metallurgist the question is invested with much importance at the present moment; for within the last seven years the iron manufacturers engaged in smelting the ore found so abundantly in the Cleveland Hills, have succeeded in reducing their consumption of fuel by about 30 per cent. on a given weight of metal produced. This change, one of national importance, has been accomplished by increasing the capacity of their furnaces, and by raising the temperature of the blast. Calculated upon the quantity of pig iron manufactured in their district alone, this represents something like a saving of one million tons of coal a year. This is exclusive of about 750,000 tons annually economised by the Cleveland smelters by profiting from the experience of the South Wales ironmasters, who had already improved, and universally applied, the French invention of using the waste gases for compressing and heating the air used in the operation.

Encouraged by previous success, the owners of ironworks in the North of England are, in some instances, still adding to the dimensions of furnaces already of colossal size; at the same time they are still seeking to increase the temperature of the blast to a point apparently limited only by the power of the combustible employed, or by the capability of the material composing their apparatus to resist its effects.

Although the increase in production from each furnace by no means corresponds with the additional cost, consequent upon this change of construction, the value of the fuel economised has been such as amply to compensate for the increase of capital now required in plant to produce a given quantity of iron.

Apart from practical difficulties which may beset the use of furnaces enlarged beyond a certain size, it is obvious there is a positive loss in an expenditure on erections which do not ameliorate the operation, or yield an adequate increase of work. The

same objection is equally applicable to heating the blast beyond that point where the additional temperature may be rendered useless, from the nature of the chemical action involved in the process.

Upon these two points some diversity of opinion exists in the minds of the manufacturers themselves, who therein, up to this time, have received no assistance from men of purely scientific pursuits. In the absence of such help, the following pages are offered as a contribution to what has been already written on this very important branch of British industry, for the use of those who feel an interest in the subject.

As is well known, ores of iron are rarely obtained so pure that the smelting process is not accompanied by the generation of a considerable weight of earthy silicates, known at the works under the names of cinder or slag, produced by the earthy constituents of the materials, with, and sometimes without, the addition of a flux, which is usually lime.

It is very possible that the presence of this foreign matter may, by varying the molecular condition of the iron oxide itself, greatly influence the character and rapidity of the changes produced in the furnace. Certain it is that different ores, all containing the metal as peroxide, are very differently affected on being submitted to agencies resembling those they encounter in the blast furnace. A similar diversity of behaviour, however, marks the conduct of pure Fe_2O_3 according to the manner in which it is prepared; hence it seems probable that to changes in molecular structure in the ore, and not to the character of the earthy impurities, must be ascribed the differences above mentioned. Under these circumstances, the formation and composition of these silicates will not be considered as necessarily holding any place in the present work.

The fact also that every variety of peroxide of iron is not similarly affected by heated carbonic oxide, renders caution necessary in attempting to draw general conclusions, as well as in questioning the results obtained by other observers, particularly when the ores under treatment are not precisely the same in each case.

The difficulty connected with an enquiry respecting the reductibility of ores of iron is further enhanced by the next to impossibility of maintaining over a period of several hours a perfectly constant temperature. Not only does even a very trifling variation in the heat materially alter the nature of the action of carbonic oxide on

an oxide of iron, but the rate at which the current is passed over the ore, or metallic oxide, has a marked influence on the character of the result.

Although the behaviour of various ores in connection with the process of reduction has formed the subject of enquiry, my chief attention has been directed to ascertaining the properties of the ironstone of the Cleveland hills during its passage through the blast furnace.

In composition this ore exhibits great variety; but the following analysis of specimens, in the raw and calcined state, will give a general idea of their usual constituents:—

	Raw Stone.	Calcined Stone.
Fe_2O_3	2·60	... ... 66·25
Fe O	38·06	
Mn O	·74	
Mn_3O_4		... ... ·65
Al_2O_3	5·92	... ... 7·72
Ca O	7·77	... ... 6·46
Mg O	4·16	... ... 4·78
Ka_2O	tr.	... ... ·02
CO_2	22·00	
H_2O	4·45	
SiO_2	10·36	... ... 11·87
S	·14	
P_2O_5	1·07	... ... 1·13
SO_3		... ... ·90
	97·27	99·58

SECTION II.—FORMATION OF CARBONIC OXIDE IN THE BLAST FURNACE.

To the generation of carbonic oxide we are indebted for the heat by means of which the metal and slag are fused in the hearth of the furnace, and by the action of this gas on the ore is produced the chemical change or changes which reduce the iron to its metallic condition. A few words, therefore, on the circumstances attending the formation of this agent, constitute an obvious link in the chain of evidence we are about to consider.

The blast furnace for the present purpose may be regarded as a circular column, swelling in diameter from both extremities. Its height varies from 30 to more than 100 feet, and its capacity from a few hundred to above 30,000 cubic feet.

Down this column, as the blast acts on the incandescent carbon at the lower extremity, the coke or charcoal travels, meeting on its way, in the form of gas, almost all the carbon which entered into the composition of the fuel previously consumed; the exception being the small quantity which is dissolved by the iron.

The opinion commonly received, up to a recent period, is that the first action of the carbon upon the blast converts all the oxygen of the latter into carbonic acid, which gas meeting, on all sides, fuel in an intensely heated state, is instantaneously resolved into carbonic oxide. It is difficult to say what has given rise to this view of the method in which oxygen unites with carbon in the blast furnace, for none of the analyses found in works on the subject appear to countenance the explanation formerly adopted. Within two feet of the tuyeres, according to those analyses, the gases contain the carbon almost exclusively as CO, and that it should exist as CO_2 lower down, appears to have been inferred rather than proved.

Professor Tunner, of Leoben, in a very interesting paper on the theory of the blast furnace,* was the first to express doubt on the mode of action just referred to. He states that the gases of the Wrbna furnace, in Styria, taken at a distance of ·08 metres (3·12 Eng. ins.) above the tuyeres, are so rich in inflammable gas that they are employed to illuminate the casting house at night. In this instance, the fuel employed is charcoal; but the same brilliancy of flame mentioned by M. Tunner, which attends the combustion of gas taken from the immediate neighbourhood of the tuyeres at coke furnaces, cannot have escaped the attention of any observer.† This gentleman found, at a point ·105 metre (4·09 Eng. ins.) from the mouth of the blast pipe, the gaseous contents of the furnace were almost exclusively atmospheric air.

Having regard to the velocity with which the gases are passing from the point where all the atmospheric oxygen is unchanged to

* Translation in "Revue Universelle des Mines, de la Metallurgie, &c.," 1er Semestre, 1860.

† It is almost needless to say that the brightness of the flame must be due to foreign matter contained in the gas, pure carbonic oxide possessing but small illuminating power.

that where this element exists as CO, the distance being only a few inches, the collection of samples with a uniform composition would appear almost hopeless. Practically, the real question is, does carbon, by its conversion into CO, afford heat of such intensity as to be able to fuse the iron under its influence. If such were not the fact, then the zone of fusion would be confined to that space where a considerable quantity of the carbon exists as carbonic acid, which space is so small that its position has not hitherto been determined.

Against the hypothesis that the hearth of a furnace requires such a heat as that produced by the conversion, or partial conversion, of C into CO_2, we have the observed fact that even in a cold blast furnace fusion takes place where no carbonic acid is found to exist; but besides this, it is well known that the heat evolved by the generation of CO is amply sufficient for melting both slag and iron.

Failing any means by which the temperature of different points of the interior of a furnace near the tuyeres can be ascertained, steps were adopted for judging of the heat of the inside by measuring that of the outside. For this purpose, holes two inches deep were bored in the wall, forming the crucible, of a hot blast furnace, at Wear Ironworks, in three different tiers, there being four holes in each tier, and each hole midway between two tuyeres. Corks were placed at the mouth of the holes, tightly fitting in which was a thermometer. The following table exhibits the readings taken upon three different days, no change having been made in the proportions of the minerals used.

EXPERIMENT 1.*

	Hole.	Tier 15 in. below tuyere.	Tier 13 in. above tuyere.	Tier 34 in. above tuyere.
First Day.	No. 1	176°C.	141°C.	141°C.
	2	192°	138°	160°
	3	177°	160°	169°
	4	195°	159°	138°
	Average	185°=365°F.	150°=302°F.	152°=305°F.

* All Experiments will be numbered consecutively, for convenience of reference.

EXPERIMENT 2.

	Hole,	Tier 15 in. below tuyere.	Tier 13 in. above tuyere.	Tier 34 in. above tuyere.
2nd Day.	No. 1	171°C.	120°C.	
	2	198°	138°	Not
	3	168°	143°	taken.
	4	193°	119°	
	Average	183°=361°F.	130°=268°F.	

EXPERIMENT 3.

3rd Day.	No. 1	176°C.	119°C.	141°C.
	2	179°	140°	174°
	3	183°	140°	185°
	4	201°	130°	145°
	Average	187°=368°F.	132°=270°F.	161°=322°F.

The strength of the masonry, 4 feet 10 inches when built, and probably now of unequal thickness, from unequal wear, prevents perfect uniformity in the indicated temperatures. The results, however, seem to prove that near the tuyeres is a zone somewhat cooler than that immediately above and immediately below it. Were the blast, within a foot or so of its entry into the hearth, converted into carbonic acid, this ought to be the zone of greatest heat; but, on the other hand, if carbonic oxide is the gas generated by the combustion of the coke, the pouring in of so large a body of air will probably, near its points of entrance, somewhat lower the temperature.

At the WEAR FURNACE, the tuyeres are so placed that the air enters at four orifices, separated by distances of four feet. At one of these the blast was shut off, so that on each side, and four feet off, the air was entering at the adjoining tuyeres. Samples of gas were then drawn off from the central orifice by means of a tube, and submitted to analysis. This was done upon five different days, with the following results, which were obtained by the volumetric process employed by Bunsen :—

	Exp. 4.	Exp. 5.	Exp. 6.	Exp. 7.	Exp. 8.
CO_2	·76	1·1	0·8	1·8	1·7
CO	37·60	31·7	33·3	35·2	35·0
H	—	·4	1·0	—	·3
N	61·64	66·8	64·9	63·	63·0
	100·	100·	100·	100·	100·

There remains another circumstance which may be adduced in favour of the hypothesis that CO, and not CO_2, is the chief, if not the exclusive, and immediate product of the action of the blast on the fuel. Heated carbon undoubtedly possesses great power in bringing down C from its highest to its lowest state of oxidation; but as will be hereafter seen, this power is enjoyed to a much greater extent by metallic iron of that form in which it comes down to the tuyere of a blast furnace. If, then, CO_2 to any great amount had to be reduced to the state of CO, in so restricted an area, in so brief a space of time, and so near the point of fusion, we ought to expect some notable quantity of Fe to pass into the state of oxide, of which oxide at least a part would pass into the slag, where, when a furnace is making foundry iron, at all events, a mere trace only is to be found. The experiments of M. Tunner would go to prove the great doubt which exists as to CO_2, in the first instance, being generated in any quantity by the action of the blast on the fuel. That the gases of a furnace, near the tuyeres, if they ever are charged with CO_2, speedily lose it, is clear, both from the analyses of those of the Wrbna furnace, and those of the Wear just quoted. The same may be said of the furnaces at Clerval and Séraing, in which, close to where the blast enters, Ebelmen gives ·93 per cent. of CO_2 at the former, and none at the latter.

The facts, and the figures already quoted, will doubtless be considered as a proof that M. Tunner's opinion that the heat we have to deal with is that afforded by the combustion of the fuel into CO, is the sound one, and that carbonic acid to any great extent is not the result of the blast on the fuel.

We have, then, to deal with carbonic oxide, practically free from any great admixture of carbonic acid; for out of four analyses made on as many different days at the Wear furnace, six feet above

the tuyeres, only one gave any trace of this gas. These analyses gave the following composition:—

Volumes.	Exp. 9.	Exp. 10.	Exp. 11.	Exp. 12.
CO_2	0·0 ...	0·0 ...	1·5 ...	0·0
CO	35·4 ...	34·4 ...	36·5 ...	34·8
H	·2 ...	1·3 ...	1·3 ...	·7
N	64·4 ...	64·3 ...	60·7 ...	64·5
	100·	100·	100·	100·

It is obvious, were no limestone or ore present, that with air driven through the mass of coke or charcoal required to fill a blast furnace the gas issuing from the top would be almost pure carbonic oxide, mixed with the nitrogen of the air blown in at the tuyeres, in about the proportions of 34 volumes of the former to 66 of the latter. Along with these would be small quantities of hydrogen, derived from the moisture of the blast,* some hydro-carbons given off by the fuel, and some compounds of cyanogen and ammonia generated in the furnace. Besides these substances, there are also found traces of sulphuric and hydro-chloric acids, together with various other substances, a list of which will be given hereafter.

Although both cyanogen and ammonia are capable of depriving F_2O_3 of oxygen, both these will be disregarded for the moment; and as the nitrogen is of itself inert, merely acting as a diluent, our business will be confined at present to considering the behaviour of the carbonic oxide as it ascends through the contents of the furnace.

* When coal is used in its uncoked state in the blast furnace, of course the hydro-carbons and hydrogen constitute important ingredients in the gases. Messrs. Bunsen and Playfair found as much as 20·63 per cent. in those at Alfreton, fed exclusively with raw coal.

SECTION III.—ACTION OF CARBONIC OXIDE ON IRON ORE IN THE BLAST FURNACE.

This carbonic oxide undergoes rapid, and, probably, repeated changes during its passage from the hearth upwards. It is not the mere generation, once for all, of carbonic acid by the reduction of oxide of iron by oxide of carbon that we have to look to, but the action of a gas containing different and constantly varying proportions of the compounds of carbon and oxygen at different temperatures on carbon, iron, and the oxides of this metal, which invests the enquiry with some degree of complication and difficulty.

The explanation hitherto accepted as the *rationale* of the process of reduction, is that the oxide of iron, after entering the blast furnace at the upper part, commences to part with its oxygen as soon as it is sufficiently heated. The temperature at which deoxidation sets in has been differently estimated by different experimenters.

M. Ebelmen permitted samples of ore to descend at the same rate as the contents of the furnace, in a piece of suitably constructed apparatus, which enabled him to expose the specimens under examination to the action of the gases, the extent of which was ascertained by withdrawing the apparatus.

M. Tunner introduced an improvement upon this method of procedure; for by placing metallic alloys of different known degrees of fusibility in the apparatus, he was enabled to judge of the temperature to which the fragments of ore had been submitted. The instrument, as employed by this gentleman, consisted of a small box of stout wrought iron, with a moveable cover, so constructed as to prevent the solid materials in the furnace entering the box, but permitting the gases, which had access through numerous holes in the bottom, to pass over the ore before leaving the apparatus.

I have attempted to give a tabulated statement, showing where deoxidation commences, and at what rate it proceeds, according to the two authorities just quoted.

Table Showing Rates of Deoxidation, &c.

Authority	Ebelmen.*	Tunner.†	Tunner.†
Furnace	Clerval.	Wrbna.	St. Stephan.
Temperature of Blast	180°C.	200°C.	200°C.
Ore, Description of, used	Supposed pisolitic & hydrated Fe_2O_3	Calcined spathose ore.	½ calcined spath. ½ argillaceous.
Ore, kilo. per 100 kilo. pig	381	200	281
Flux, kilo. do.	37	10	13
Description of Flux	Limestone	Grauwacke.	Limestone.
Charcoal, kilo. per 100 kilo. Pig	148	70	95 to 100
Make of Pig per 12 hours kilo	4357 kilos.	12009 kilos.	5827 kilos.
Quality	Grey.	White.	Grey.
Ore commences to lose O	in 2 hours.	1 hour.	not given.
Depth from top of Fur.	2·50 metres.	4·8 metres.	4·6 metres.
Temperature	not red hot.	650°C.	under 600°C.
Vol. CO_2 per 100 vol. CO	60 vol.	150 vol.	supposed 100 vol.
First sign of Metallic Fe	in 5 to 6 hours.	1⅔ hours.	6 hours.
Depth from top	6 to 7 metres.	7 metres.	9¾ metres.
Temperature	red hot.	875°C.	820°C.
Vol. CO_2 per 100 vol. CO	0	Supposed 50.	not given.
50 *per cent. of O removed in*	6½ hours.	2½ hours.	6½ hours.
Depth from top	7½ metres.	8½ metres.	10 metres.
Temperature	mal. iron softened.	1000°C.	840°C.
Vol. CO_2 per 100 vol. CO	0	8	not given.
Complete Reduction in	not given.	3 to 4 hours.	supposed 9 hours.
Depth from top	do.	10⅔ metres.	11½ metres.
Temperature	do.	1450°C.	supposed 1200°C.
Vol. CO_2 per 100 vol. CO	do.	About 50 vol.	not given.
Time of Ore passing through Furnace		4½ to 5 hours.	12 hours.

* Percy's Metallurgy.

† Theorie des hauts-fourneaux. Translation in "Revue Universelle des Mines de la Metallurgie," &c.

M. Scheerer* gives the following as his ideas on the rate of reduction, and the temperature at which it is completed. His opinions are based on the recorded experiments of M. Ebelmen, at the furnace at Veckerhagen, blown with air heated to 150° to 300°C., and worked with charcoal.

At 17¾ feet above the tuyeres, the temperature is considered as 300°C. (572°F.), where the gases had a composition of N 62·34. CO_2 8·77, CO 24·20, H_2 C_2 3·36, H 1·33 by vols.; the ore suffers no change beyond the loss of water and absorption of heat.

Between this and the top of the boshes, in which region the temperature gradually rises from 300°C. (572°F.) to 1000° to 1200°C. (1830° to 2190°F.), reduction begins and is completed.

In a recent publication by M. C. Schinz, of Strasbourg,† he states that by preparing a gaseous mixture resembling, so far as CO and N are concerned, the mixture found in the blast furnace, the following was the rate of reduction. The gas consisted of 34·65 vols. CO, to 65·35 vols. N, and the temperature was measured by a thermopile constructed by M. Schinz himself.

Ore.	Average Temperature.		Per cent. of O lost per hour.
Bohnerz	622°C.	1151°F.	0·22
Spathose	749°	1380°	0·16
Hayange Oolitic	622°	1151°	1·09
Namur do.	632°	1170°	1·78

From the preceding quotations from the labours of these continental chemists, the inference is that in the blast furnace, even when the gases consist of nitrogen and carbonic oxide without any carbonic acid being present, reduction is languid at 600°C (1112°F.); indeed, M. Tunner expresses doubt as to whether the iron ore commences to lose its oxygen under 650°C. (1207°F.)

I have somewhat carefully examined previous writings on the circumstances which are supposed to influence the action of CO on iron oxides; because upon the manner in which this duty is performed depends the success of the smelter's operations. This gas, charged with heat and endowed with reducing properties, ought not to be permitted to quit the blast furnace so long as its temperature and its power to absorb oxygen have not been exhausted, as far as the nature of the operation will permit.

* Scheerer, Lehrbuch der Metallurgie.
† Dokumente betreffend den Hohofen zur Darstellung von Roheisen.

SECTION IV.—EXPERIMENTS TO ASCERTAIN THE TEMPERATURE AT WHICH CARBONIC OXIDE COMMENCES TO ACT ON OXIDE OF IRON.

The exposure of specimens of ironstone to the escaping gases of furnaces working with closed tops having led me to question the accuracy of the conclusions arrived at by the authorities just quoted, a number of experiments were instituted, in the hope of obtaining further information with respect to the actual temperature at which deoxidation commences.

Before entering upon the examination of the action of carbonic oxide, as it exists in the gases of a blast furnace, a number of trials were made with this gas in its pure state, in order that I might learn at what temperature, and at what rate, deoxidation commences and progresses with $Fe_2 O_3$ variously prepared, and with ores of different kinds.

The CO was prepared from ferrocyanide of potassium, purified by being passed successively through KHO and $Ag NO_3$ to free it from CO_2, SO_2, and HCy. Thus obtained it exhibited no turbidity on being passed for ten minutes through lime water.

The substances operated upon, in the first experiment, were placed in a Liebig's drying tube, in which a delicate thermometer was introduced, and the whole immersed in an air-bath, by which a tolerably constant temperature could be maintained in the inside of the drying tube. Upon each trial the CO was passed, in a slow stream, sufficiently long to insure that the $Fe_2 O_3$, or ore, had acquired the temperature of the gas, and before escaping the carbonic oxide bubbled through lime water, in which the presence of CO_2 was instantly perceptible.

In order to obtain pure $Fe_2 O_3$ with some probable difference in molecular condition, specimens of this substance were prepared in the following ways:—

A. Pure precipitated $Fe_2 O_3$. Pure $Fe SO_4$ was peroxidised by $NO_2 H$, and the $Fe_2 O_3$ thrown down by NH_3. The precipitate was thoroughly washed, and ignited gently to expel $H_2 O$ of hydration.

B. Fe_2O_3 obtained by calcining crystals of pure $FeSO_4$ at a bright red heat, until all SO_3 was driven off.

C. Fe_2O_3 formed by heating to redness the product of NO_3H on wrought iron filings.

D. Roasted Cleveland ironstone. An average sample of which contained Fe_2O_3 57, and earthy matter 43 per cent.

E. A portion of D, further calcined in a muffle for six hours at a bright red heat, which, however, did not perceptibly alter its percentage of Fe_2O_3.

F. Pumice-stone, soaked in a solution of $FeSO_4$, dried and calcined in a muffle until all SO_3 had disappeared.

Substance Employed.	Lowest Temperature at which CO_2 appeared.	Temperature of marked action.
Exp. 13 Pure precipitated Fe_2O_3	141°C.=285°F.	149°C.=300°F.
„ 14 Fe_2O_3 got by calcining $FeOS_4$...	208 =407	216 =420
„ 15 Do. on Pumice-stone	211 =412	227 =440
„ 16 Fe_2O_3 from calcining $FeNO_3$...	145 =293	154 =310
„ 17 Calcnd. Cleveland ore	199 =389	210 =410
„ 18 Do. roasted six hours longer ...	200 =392	206 =402

To form some idea of the extent to which CO, at low temperatures, would remove O from Fe_2O_3—

Exp. 19.—This gas was passed over precipitated anhydrous Fe_2O_3 for two hours, at a temperature of 243°C. to 265° (470° to 510°F.). At the end of this time 19·4 per cent. of the original oxygen was removed.

Exp. 20.—The previous experiment was repeated at a temperature of 232° to 254°C. (450° to 490°F.) for six hours, which expelled 49·3 per cent. of the original oxygen.

It is worthy of remark that the formation of CO_2, proving the commencement of deoxidation, took place at a perceptibly lower temperature when a perfectly fresh specimen of oxide was used than where one was employed which had served in previous observations; a fact which shows that the very first portions of O are separated the most easily.

Exp. 21.—Thus one sample of Cleveland ore was found to commence yielding CO_2 at 389°F. (198°C.) when perfectly fresh; but after having been used for a few trials at higher and lower temperatures, the lowest temperature at which CO_2 was found to be given off was 394°F. (201°C.)

This probably arises from the alteration in the surface of the substance experimented with; to avoid error from this source, fresh specimens were always employed after one or two observations had been made.

To obtain the rate of deoxidation at various temperatures, 8·5 grammes of Cleveland calcined ore were placed in a Liebig's drying tube, kept hot by means of an oil bath. After the tube and its contents had been immersed a sufficient time to have acquired the temperature of the oil, all air being previously expelled, CO was led over the ore. The issuing gas passed through two KHO bulbs, with another bulb containing limewater, which latter, never becoming turbid, was a proof no CO_2 formed by the reduction of the ore escaped. The increase of the weight by absorption of CO_2 was noted, and the rate of reduction thereby ascertained.

	Oxygen removed per hour per 100 of ore.		O removed per hour per 100 of original O in Fe_2O_3
Exp. 22 210° to 227°C. (410° to 440°F.) ...	0·048	...	0·28
„ 23 221° to 238°C. (430° to 460°F.) ...	0·048	...	0·28
„ 24 260° to 277°C. (500° to 530°F.) ...	0·222	...	1·31
„ 25 Zinc barely melted 415°C.=779°F.	·986	...	5·80

Reference has been previously made to suceptibility of reduction being modified by differences in molecular condition of the oxide of iron or ores under examination. This is apparent in the experiments Nos. 13 to 18 just described; but inasmuch as the various trials were conducted at different times, a piece of apparatus was constructed in which several specimens could be simultaneously brought under the action of the CO, and by means of which almost identity of treatment was obtained, and more correct results, comparatively speaking, secured.

A cylindrical basin of cast iron, having an internal diameter of six inches, was made, provided with an accurately fitting cover, which, by means of a powerful screw, was pressed into a bevilled seat ground air tight. This cover had fastened into it two tubes,

one to admit the gas and the other to permit its escape. The basin was placed within another of such dimensions as allowed the former to be immersed in a bath of melted lead, which surrounded the inner vessel on every side to the extent of three inches. The lead bath was maintained, as nearly as possible, at a constant temperature, by help of a coke fire regulated by a damper, and the mass of metal heated being considerable the temperature was not affected by small fluctuations of the combustion in the furnace.

Weighed porcelain trays containing the substances to be experimented on, were placed on the flat bottom of the basin, along with a similar dish provided with pieces of pure lead, zinc. and antimony, which metals, by their fusion or otherwise, indicated the maximum temperature attained during the trial. The substances were spread on the dishes in layers about one-tenth of an inch in thickness, so as to secure free access for the gas.

The temperature of the escaping gases of the blast furnaces in the North of England never much exceeds, on an average, that of melting zinc, and in the case of those of larger dimensions the gases scarcely reach that of melting lead. In the lead bath, the melting point of the former metal (412°C.=774°F.) was usually aimed at; and at this, judging by the behaviour of the lead in the bath when a fresh surface was brought in contact with the air, there was no difficulty in maintaining it uniformly.

After exposure to the gas, the basin was removed from the bath, and an atmosphere of the CO retained in its interior, under pressure until it cooled, so as to avoid all chance of reoxidation.

The products were then weighed and analysed. The method adopted in the analyses of the partially reduced ores was as follows:—A known weight of the substance was heated in a current of oxygen at first gently, and subsequently to full redness. In case the specimens were known to contain carbon, a tube, containing red hot oxide of copper was placed in front, so as to ensure the conversion into CO_2 of any CO that might be produced, and the CO_2 evolved was collected and weighed. The residual substance uniformly contained the whole of its iron in the state of Fe_2O_3, provided sufficient care were taken not to raise the heat so high as to frit the lower oxides of iron produced before complete peroxidation took place; the per centage of iron in this product being then determined (or known from the original composition of substance

used), the amount of "earths" contained in the specimen analysed was known, the oxidized product being regarded as made up solely of Fe_2O_3 and "earths;" hence, by subtracting from the weight of substance taken for analysis the sum of the earths, the Fe present, and the C in the CO_2 produced by the combustion, the residual oxygen associated with the iron was known: and, as (in cases where substances containing all the iron as Fe_2O_3 were employed), the original oxygen was $\frac{3}{7}$ of the iron contained, the amount of oxygen lost by the exposure was easily calculated.

In some instances, the amount of reduction was ascertained by dissolving a known weight of product in acid, and titration by permanganate; but this method was rarely resorted to, save as a check upon the results got by the former method.

Direct observations showed that even spongy iron could be perfectly converted into Fe_2O_3 by combustion in oxygen, by suitably regulating the temperature.

The following results were obtained in the apparatus just described by exposing the substances enumerated below for seven hours to the action of pure CO, zinc being melted, but antimony not affected.

	Substance employed	Gas used.	Temp.	Original O removed.
Exp. 26.	Calcined Cleveland ore.	CO	a little above 417°C. or 782°F.	9·4 per cent.
„ 27.	Pumice-stone with Fe_2O_3	„	„	23·8 „
„ 28.	Calcd. Fe SO_4 (Fe_2O_3)	„	„	61·7 „
„ 29.	Fe_2O_3 precipitated	„	„	66·7 „
„ 30.	Fe_2O_3 from nitrate	„	„	72·7 „

Exposure for 7½ hours to pure CO, at a temperature of softened zinc, about 410°C. (770°F.) in the lead bath.

		Original O removed.
Exp. 31.	Lancashire hæmatite, con. 40·3 per cent. iron	37·1 per cent.
„ 32.	Fe_2O_3 from nitrate	59·9 „

Exposure for 7½ hours to pure CO, at a temperature of softened zinc, about 410°C. (770°F.) in the lead bath.

					Original O removed.
Exp. 33.	Calcd. Clev. ore, containing	40	per cent.	Fe	20·7 per cent.
„ 34.	Calcd. spathose ore	„ 51·7	„	„	28·4 „
„ 35.	Lanch. hæmatite	„ 40·3	„	„	57·4 „

Exposure for 6 hours to pure CO, at a temperature of about 410°C. (790°F.) in the lead bath.

				Original O removed.
Exp. 36.	Calcd. Clev. ore, containing	40 per cent. Fe		37·3 per cent.
„ 37.	Lanch. hæmatite „	66·6 „	„	35·9 „
„ 38.	Elba specular ore „	66·8 „	„	16·8 „
„ 39.	Calcd. spathose ore „	51·7 „	„	15·4 „
„ 40.	Pure Fe_2O_3 precipitated	70·0 „	„	49·2 „
„ 41.	Do. cal. $FeSO_4$	70·0 „	„	60·8 „

These experiments are sufficiently instructive in pointing out the influence which molecular structure is considered to exert in the rapidity of deoxidation. As a still more striking example of this, may be quoted—

Exp. 42, in which Cleveland calcined ore, weighing 3·33 grammes, was exposed for 20½ hours to a current of pure CO, during which time it only lost 13·65 per cent. of its original oxygen, the temperature being maintained in an air bath at 216°C. (420°F.), whereas precipitated anhydrous Fe_2O_3, at an average temperature of 243°C., lost 49·3 per cent. of its oxygen in 6 hours.

In comparing the results obtained in the last six experiments with those of experiments Nos. 32, 33, and 34, it will be perceived that although the temperature in each case was nominally the same, viz., 410°C. (770°F.), and although the exposure, when six specimens were employed, lasted six hours, and in the other cases seven hours, the calcined Cleveland stone, taken from the same sample, lost 37·3 per cent. of its original oxygen in the shorter time, and only 20·7 per cent. in the longer; while, on the other hand, the calcined spathose ore gave off 28·4 per cent. of its oxygen in the longer, and only 15·4 per cent. in the shorter, period.

Conceiving that this difference might be due to the rate at which the CO had been passed through the apparatus, viz., 63 litres in six hours, or possibly to some slight alteration in temperature of a local character, the previous set of experiments was repeated, samples from the same specimens being used, and each sample of each particular substance placed in the same position in the lead bath as that occupied by its predecessor.

The same temperature was aimed at, viz., 410°C.; but in this case 245 litres of Co. were passed through in the six hours.

				Original O removed.
Exp. 43.	Calcd. Clev. ore, containing	40 per cent. Fe	...	50·6 per cent.
„ 44.	Lanch. hæmatite „	66·6 „	...	70·9 „
„ 45.	Elba specular ore „	66·8 „	...	18·1 „
„ 46.	Calcd. spathose ore „	51·7 „	...	41·9 „
„ 47.	Pure Fe_2O_3 precip. „	70·0 „	...	80·0 „
„ 48.	Do. from cal. $FeSO_4$	70·0 „	...	72·5 „

Compared with each other, the percentage of original oxygen lost is as follows:—

	Clev.	Lanc.	Elba.	Spathose.	Fe_2O_3	Fe_2O_3	Average.
Slow current of CO ...	37·3	35·9	16·8	15·4	49·2	60·8	35·9
Rapid do. ...	50·6	70·9	18·1	41·9	80·0	72·5	55·7

The probable cause of this will be better understood when we come to consider the effects of carbonic acid upon metallic iron. In the meantime it must be recollected what very trifling circumstances greatly modify the action we are considering. So far as the temperature is concerned, the test samples of metals were placed in the centre, and the specimens of iron compounds surrounding them in a circle; and when it is stated that zinc was melted, it means that antimony, the fusing point of which is only 33°C. (60°F.) higher than that of zinc, was not affected.

SECTION V.—BEHAVIOUR OF OXIDE OF IRON IN CONTACT WITH CARBONIC OXIDE AT A RED HEAT.

Trials were then made with higher temperatures to ascertain the increase of rapidity in the rate of reduction of iron oxide by means of pure CO.

Exp. 49. Cleveland calcined ore lost, at a heat visibly red in daylight, 63 per cent. of its original oxygen in 8 hours.

Exp. 50. The same substance, at a bright red heat, had lost nearly 90 per cent. of its oxygen after an exposure of $3\frac{3}{4}$ hours to the action of CO.

In the case of Exp. 50 nearly the whole of the iron was obtained in the condition of metal, and accepting Fe O as the lowest state of oxidation in which Fe can exist, something like one-fourth of the iron in Exp. 49 must have been in the metallic form. It will

shortly be shown, however, that there are reasons for supposing the formation of an oxide Fe_3O by the action of CO on Fe_2O_3.

The removal of a small quantity of oxygen from Fe_2O_3 may indicate the existence of metallic iron, or merely a lower state of oxidation of a larger quantity of ferric oxide, which has been exposed to the reducing influence of CO. In order to distinguish between these two results, several careful experiments were made by Dr. Wright on the action of pure iodine on Fe and its oxides, which are given below.

Exp. 51. Pure Fe_2O_3 was digested with iodine and cold water; no Fe dissolved even after 24 hours.

Exp. 52. Pure Fe_2O_3 was reduced in H until no more H_2O was produced. The metallic iron was then digested with iodine and water. All the residue was dissolved in one hour, with the exception of a small quantity of brown powder, (Fe_2O_3) weighing only 0·2 per cent. of the original substance.

Exp. 53. Pure Fe_2O_3, partially reduced in H, and containing 81·4 per cent of Fe, was digested as before. A constant quantity (12·5 per cent) of Fe was dissolved, whether the digestion in iodine and water was continued for 1 or for 18 hours. Further, the quantity dissolved was not altered by adding a large excess of Fe_2O_3 to the partially reduced oxide, and then digesting as before.

Exp. 54. Another sample of Fe_2O_3, partially reduced by H, had 5·1 per cent. of Fe dissolved out by digestion continued for one hour with iodine and cold water, and 4·7 per cent. more, making 9·8 per cent. in all, on being boiled for five minutes.

Exp. 55. Fe SO_4 was precipitated by KHO in excess, and washed very rapidly. The hydrated Fe O (partially converted into Fe_2O_3), on being digested with iodine and cold water, yielded a large quantity of iron in solution after one hour. When boiled for ten minutes, the portion insoluble in iodine only contained traces of Fe O. The same result was obtained after 18 hours' digestion in the cold.

Exp. 56. Several samples of Fe_2O_3, partially reduced by CO, until the resulting product exhibited a composition intermediate between Fe O and Fe_2O_3, yielded no iron in solution on digestion with iodine and cold water for some hours; but considerable quantities of iron were obtained dissolved, if boiled or only heated to 50°C.

Exp. 57. By the action of a mixture of CO and CO_2, in equal volumes at a bright red heat, upon spongy iron (produced by reduction of pure Fe_2O_3 in hydrogen), an oxide is obtained exhibiting almost exactly the composition of anhydrous Fe O. On digesting this with iodine and cold water, no trace of metal was dissolved.

Exp. 58. Precisely the same results were got with the oxides of nearly the same composition obtained (mixed with earthy matters), by subjecting Lancashire hæmatite, calcined Cleveland, spathose ores, and pure Fe_2O_3 (not reduced in hydrogen), to the action of the same gas at the same temperature.

These experiments indicate that:—

1st. Metallic Fe, in its spongy state, is readily dissolved in one hour by iodine and cold water.

2nd. Peroxide of iron is wholly unaffected by similar treatment.

3rd. Protoxide of iron, when anhydrous, the state in which it is obtained by the partial reduction of Fe_2O_3, is almost unaffected by prolonged digestion in the cold, but is more or less soluble if heat is applied during the digestion. Oxides, intermediate in composition between Fe O and Fe_2O_3, behave precisely as mixtures of Fe O and Fe_2O_3.

4th. Hydrous protoxide of iron is readily dissolved in the cold, the action brobably being—

$$3\,FeO + I_2 = FeI_2 + Fe_2O_3,$$

inasmuch, as the undissolved Fe_2O_3 always contained rather more than twice as much iron as the dissolved part, the excess being derived from peroxidation while washing the precipitate.

To ascertain whether metallic iron was present in the iodine solutions obtained in the manner described, the filtered liquid was boiled with NO_3H and H Cl, and then supersaturated with NH_3. If no Fe was found in solution, it was inferred that iron, in the form of metal, was absent; but it is evident from experiments 54, 55, and 56, that hydrated and even anhydrous Fe O may be attacked by the iodine solution under the influence of warmth, and, therefore, that the converse cannot with certainty be inferred. What, however, is considered as proved is, that if no Fe is dissolved, none of this substance can exist in the metallic condition.

It is a matter of interest for more reasons than one to ascertain with how small a loss of oxygen, and at how low a temperature,

metallic iron can be produced in an oxide which has been exposed to the action of CO.

Exp. 59.—Calcined Cleveland ore was exposed for 20½ hours in the air bath arrangement to CO, at a temperature of 213° to 221°C. (415° to 430°F.) The loss of oxygen at the end of the trial amounted to 13·55 per cent. of that required to form Fe_2O_3. In this case, not a trace of metallic iron was generated.

Exp. 60.—Precipitated anhydrous Fe_2O_3 was similarly exposed for only two hours, when 19·3 per cent. of its oxygen was expelled. The temperature varied from 243° to 265°C. (469° to 509°F.) In it 5·7 per cent. of the iron was metallic.

Exp. 61.—Same Fe_2O_3 as in last experiment was heated for six hours in a current of CO to a temperature of 232° to 254°C. (451° to 486°F.) The residue contained 15·6 per cent. of its Fe as metal, while only 50 per cent. of its oxygen was removed.

These experiments prove that metallic iron may be generated before the whole of the Fe_2O_3 is converted not only to Fe O, but even so low as Fe_3O_4, and also that pure oxide affords metallic iron sooner than Cleveland ore.

It was noticed in several instances where Fe_2O_3 had been exposed to the action of CO that the amount of residual oxygen bore to the iron *insoluble in iodine* and cold water a ratio less than that required to form protoxide. Thus the following numbers were obtained:—

	Time of Exposure.	Temperature.	Substance exposed.	Residual O per 100 of Fe insol. in iodine.
Exp. 62.	7 hours ...	Zinc melted. Sb not.	Fe_2O_3 from calcd. nitrate. ...	13·0
,, 63.	7 ,, ...	do.	Precipitated Fe_2O_3.	15·0
,, 64.	7½ ,, ...	do.	Fe_2O_3 from nitrate	17·4
,, 65.	7½ ,, ...	do.	Hæmatite 40·3 per cent. Fe ...	18·8
,, 66.	7 ,, ...	do.	Calcined Fe SO_4	20·4
,, 67.	6½ ,, ...	do.	Precipitated Fe_2O_3	24·8
,, 68.	10 ,, ...	do.	do.	25·0
,, 69.	15 ,, ...	do.	do.	25·1

The oxygen required to form FeO is 28·6 per 100 Fe; hence the above numbers lead to the conclusion that a *lower oxide* than FeO must have been produced. In experiments 62 and 63, the residual oxygen is sensibly that required to produce Fe_2O (14·3 oxygen per 100 Fe), the difference not being more than might fairly be attributed to experimental errors, all of which are necessarily accumulated in the determination of residual oxygen got by

difference: the higher numbers are easily explainable on the supposition that variable mixtures of Fe_2O and FeO were produced. It will be shown hereafter, that when CO acts on the oxides of nickel and cobalt, there is reason for supposing that suboxides Ni_2O and Co_2O are produced.

SECTION VI.—ACTION OF CARBONIC ACID ON METALLIC IRON.

Sufficient has been said to prove that pure CO commences to reduce Fe_2O_3 at a very low temperature (about 140°C.), and that at a moderate red heat the greater part of the oxygen contained is rapidly removed. In all the trials referred to, the current of CO was such, that the CO_2 generated was more or less speedily removed from contact with the oxide or ore, so that in effect the results were the same as if only a trifling quantity of CO_2 had been present.

Were there no such removal, it is obvious the reducing influence of the CO would quickly be diminished by the accumulating CO_2, generated by the former gas on the Fe_2O_3; because, as is well known, the power of CO_2, under suitable conditions as to temperature, to oxidise iron is very marked.

This faculty of CO_2 to confer O on Fe is an impassable barrier to the complete reduction at any temperature above 400°C of Fe_2O_3, by its actual equivalent of Co, the equation

$$Fe_2O_3 + 3\,Co = 2\,Fe + 3\,CO_2$$

being, under the circumstances, a chemical impossibility. It is, therefore, a question of the highest practical importance to ascertain the laws which govern these antagonistic forces, regulating as they must do the proportion of carbon in the gases; and, therefore, the consumption of fuel required for smelting a given weight of iron.

The first step in the proposed enquiry is to ascertain the temperature at which the oxidising power of CO_2 commences to be exercised.

Exp. 70.—Precipitated Fe_2O_3 was wholly reduced in H, and then sealed up in a hard glass tube from which all air had been expelled by a current of dry CO_2. It was then immersed in an air bath for two hours, having a temperature of 249° to 265°C. (480°

to 509°F.) No CO could be detected in the gas, showing that no change had been effected in the CO_2.

Exp. 71.—CO_2 was passed over spongy iron in a Liebig's tube heated in an air bath up to 299°C. (570°F.), without any change being observed.

Exp. 72.—When the temperature, however, is raised to that of melting zinc, 417°C, (782°F.), dry CO_2 is rapidly decomposed by spongy iron. 2·85 grammes of the metal were placed in a tube and exposed at this temperature to a gentle stream of CO_2, all air being previously expelled from the apparatus. In 40 minutes 100 cc of gas were collected, which consisted almost entirely of CO. It was found to contain 96 vol. of CO and 4 vol. of CO_2, The iron gained 2·6 per cent. in weight, while that due to the above weight of CO corresponds to 2·5 per cent. on the Fe.

Exp. 73.—On repeating the above experiment at a red heat, the resulting gas consisted of a mixture of CO_2 and CO, varying according to the velocity of the current of CO_2 passed over the spongy iron. With a slow stream, 100 vol. of the resulting gas was composed of 60 vol. CO_2 and 40 vol. of CO.

SECTION VII.—ACTION OF MIXTURES OF CO AND CO_2 ON Fe.

From what has preceded, we may assume that deoxidation of Fe_2O_3 by CO commences at about 140° to 200°C., according to the substance used, while oxidation of spongy iron does not set in until the temperature rises to a little above 400°C.

The action between metallic iron and CO_2, at low temperatures, is thus less energetic than that between CO and Fe_2O_3; but as the heat is increased the power of both actions becomes stronger. Eventually, however, the oxidizing influence of the CO_2 predominates, from the circumstance that high temperature favours it more strongly than happens with the reducing agency of CO.

The rate of these changes I have already shown in a paper read before the Iron and Steel Institute,* and the views then published have been confirmed by further trials. The two following experiments show conclusively that while a given proportion of CO can

* "On the Development and Appropriation of Heat in Furnaces of Different Dimensions." Transactions Iron and Steel Inst., Sept. and Oct., 1869.

hold in check the oxidizing power of CO_2 on iron, at one temperature, it ceases to be able to do so at another.

Exp. 74.—A mixture of 100 vol. CO and 98 CO_2 was passed over Cleveland ore, which had been completely reduced by H, and then containing 48 per cent. of iron. The temperature was that of melting zinc (417°C.), at which (Exp. 72) CO_2 alone is rapidly decomposed by spongy iron. The CO was found to have completely arrested the oxidation of the metal.

Exp. 75.—The same mixture as that of the previous experiment (100 vol. CO, 98 vol CO_2) was conducted over reduced Cleveland ore at a full red heat. In half an hour the iron had absorbed oxygen equal to 13·8 per cent. of that existing in Fe_2O_3.

Diminishing or increasing the CO_2, of course, affects in a corresponding manner the amount of oxidation, provided the temperature in each case be maintained at the same point.

Substance.	Vol. CO_2 per 100 CO.	Temperature.	Time of Exposure.	Absorbed oxygen per cent. of that existg. in Fe_2O_3.
Exp. 76. Reduced Clev. ore ...	616 ...	full red...	¾ hour...	43·1
Exp. 77. From same sample ...	37 ...	„ ...	½ „ ...	3·06

The following trials were made to find out the circumstances under which a constant composition of gas was obtained at different temperatures.

Exp. 78.—Pure CO_2 was passed over spongy iron, obtained by reducing Fe_2O_3 by means of H. At a low red heat it was not found practicable to convert more than 40 per cent. of the issuing gas to the state of CO, or in the ratio of 100 CO to 150 CO_2.

Exp. 79.—7·9 grammes of calcined Cleveland ore, perfectly reduced by H, containing 48 per cent. Fe, were placed in a platinum boat, and heated to bright redness in a porcelain tube. At each end of the tube was a mercurial gasholder, containing about 1200 ccs, so that by depressing one gasholder the gas it held passed over the heated ore and raised the other. In this way the 1200 ccs of gas was exposed to the action of the iron oxide five times every hour, by alternately raising and depressing the gasholders. The usual precautions were taken to exclude, as far as possible, all air previous to commencing the experiment. Samples of the resulting gas were drawn at stated periods, and these on analysis, gave the following results:—

	Original Gas.	After 2 hours.	4 hours.	6 hours.	7½ hours.	11½ hours.	13½ hours
CO_2	36·9	35·9	31·7	30·5	31·2	30·9	31·1
CO	59·7		64·8			65·3	
Air	3·4		3·5			3·8	
	100·		100·			100·	

The original reduced ore increased in weight 1·67 per cent., and as it contained, previous to the experiment, 48 per cent. of Fe, this represents 3·5 of O per 100 of metal. Hence, the metal had absorbed 8·2 per cent of the oxygen required to convert it into Fe_2O_3. Calculated upon the amount of CO_2 transformed into CO the absorption of O only corresponds to 2·5 per 100 of Fe, the difference no doubt being due to air, and possibly a trace of aqueous vapour present.

Exp. 80. The previous experiment was repeated, with this difference, that the porcelain tube containing the reduced ore was placed in a coke furnace, and heated to a temperature approaching whiteness. All moisture was avoided, and air carefully expelled by repeatedly filling and emptying the gasholders, using the same composition of gas as that which had to serve in the trial.

	Original Gas.	After 1 hour.	2 hours.	5 hours.	6 hours.	7 hours.
CO_2	36·5	25·9	10·2	13·4	9·9	10
CO	62·2					89·2
Air	·3					·8
	100·					100·

Just before the fifth hour fresh coke was put on the furnace, which lowered the temperature of the tube, and the effect is visible in the increased percentage of CO_2, which, however, disappeared as soon as the heat rose.

The reduced ore gained in weight 2·46, which is equal to 5·1 per cent. of O absorbed per 100 of Fe. Hence, the metal had absorbed 11·9 per cent. of the oxygen required to convert it into Fe_2O_3. The oxygen corresponding to CO_2 converted into CO, represents five per cent.

Neglecting the influence which the small quantity of oxide of

iron exercised in the results of the last three experiments, the points of equilibrium arrived at are—

Low red heat... ...	150 vol. of CO_2	for each 100 vol. CO.
Full red heat... ...	47 „ „	
Approaching whiteness	11 „ „	

The manner in which the presence of a minute quantity of atmospheric O may affect the power of CO_2 to add to the O already combined with the Fe, has not in the previous experiments been taken into account. In experiment 79, the O absorbed amounted to about one-twelfth, and in experiment 80 to about one-eighth of that existing in Fe_2 O_3.

SECTION VIII.—ACTION OF MIXTURES OF CO AND CO_2 ON Fe_2 O_3.

It is easy to comprehend, from the nature of things, that as the iron approaches saturation with O, it will lose in its power to take this element from Co_2; and for the same reason, if there is an excess of ferric oxide, CO may be wholly converted into CO_2.

Exp. 81. A mixture of 100 volumes of CO, and 125 of CO_2 with 546 N, was passed slowly over a considerable quantity of calcined Cleveland ore at a little above melting zinc. The issuing gas was almost wholly free from CO. In $1\frac{3}{4}$ hours 5·25 per cent. of the original oxygen contained in the ore was driven off.

Exp. 82. A mixture of 100 vol. CO to 600 vol. CO_2, transmitted through calcined Cleveland ore in excess, at a low red heat in half an hour, removed 5·8 per cent. of the original oxygen of the Fe_2O_3.

Exp. 83. A mixture of 100 vol. of CO to about 400 of CO_2, was passed over an excess of calcined Cleveland ore. The latter lost 15·7 per cent., in one hour, of the oxygen it originally contained. The temperature was full red.

Exp. 84. 100 vol. of CO was mixed with 220 vol. of CO_2, and passed over Cleveland calcined ore in excess, at a heat just visibly red. In $1\frac{1}{2}$ hours the loss of original oxygen was 11·7 per cent.

To learn at what point of oxidation iron ceased to be affected by a mixture of CO and CO_2, these gases, in equal volumes, were passed over the following substances, with the results given:—

	Substance used.	Orig. per centage of Fe.	Temp.	Hours exped.	Oxygen per 100 Fe Lost.	Residual.	Gained
Exp. 85.	Cal. Clev. ore...	40	Bright red.	5½	14·8	28·00	
„ 86.	Lanc. hæmatite	40·3		5½	14·55	28·35	
„ 87.	Spathose ore...	32·6		4½	13·10	29·70	
„ 88.	Precip. Fe_2O_3	70·0		6	13·05	29·75	
„ 89.	Do. redcd. in H	100·0		13	...	...	28·5

In each case the operation was continued until the substance ceased to alter in weight. The amount of oxygen removed or gained was ascertained by the change in weight, and checked by a permanganate solution of known strength, required to complete the peroxidation of the product dissolved in H Cl, and again by the increase of weight the substances experienced by heating in pure O; the discrepancies between the results got by the three methods were but trifling.

In the first four of the last experiments given, 100 of Fe has lost 13·87 out of 42·8, leaving 28·93 still combined with iron. In the case of the spongy iron, oxygen has been absorbed almost exactly to the extent to which this element has been left in the oxides. Hence, at a bright red heat, in a mixture of equal vols. of CO and CO_2, an oxide containing 100 Fe and 29 O may be considered stable. These proportions are almost precisely those of Fe O, and the process described may, therefore, serve as a means of obtaining this substance in an anhydrous state.

Exp. 90. A mixture of 100 parts CO, 593 CO_2 and 20 of air accidentally present, was passed over calcined Cleveland ore, at a red heat, for half an hour: the oxygen retained in the residual substance was 94 per cent. of that originally present, 6 per cent., having been removed by the gaseous mixture.

Exp. 91. A mixture somewhat similar to that used in the last experiment (100 CO, 617 of CO_2, and 14 of air) was passed over perfectly reduced Cleveland ore, at a bright red heat, for 45 minutes; thereby oxygen was communicated to the metal in quantity equal to 87 per cent. of that required to form Fe_2O_3.

From these two experiments it appears that a mixture of 100 vols. CO and about 600 of CO_2 would be inert upon an oxide containing about 90 to 94 per cent. of the oxygen required to form Fe_2O_3 at a red heat. A closer accordance in the composition of the resulting oxide would doubtless have been obtained, had the action of the

gas been continued longer in the two cases, and had the composition of the two gases and the temperature been more nearly identical.

Exp. 92. Pure CO was passed over precipitated Fe_2O_3, at a bright red heat, for 5 hours, the resulting product being carefully cooled down in a stream of CO: the oxygen still remaining associated with the iron was found to be 1·0 per cent. of that required to form Fe_2O_3.

Exp. 93. Pure CO was passed over perfectly reduced, spongy iron, at a bright red heat, for 1 hour, and the current of gas kept up until perfectly cold: the resulting substance had taken up 1·1 per cent. of the oxygen required to form Fe_2O_3.

Exp. 94. The preceding experiment was repeated, the spongy iron being exposed for 4 hours, to a bright red heat: the oxygen taken up was 0·8 per cent. of that required to form Fe_2O_3.

These numbers (experiments 92, 93, 94) show that a point of equilibrium is arrived at when pure CO is made to act upon an oxide of iron, containing about 1 per cent. of the oxygen requisite to form Fe_2O_3.

Exp. 79 shows that the point of equilibrium is got when 47 vols. of CO_2 to 100 of CO act at a full red heat on an oxide, containing 8·2 per cent.—the oxygen required to form Fe_2O_3, while experiment 80 shows that the point of equilibrium of a mixture of 11 vols. CO_2 to 100 of CO is arrived at, at a heat approaching whiteness, when the oxide formed contains 11·9 per cent. of that required to form Fe_2O_3. Putting these several cases in tabular form:—

Expts.	90 & 91.	600 vols.	CO_2	to 100 of CO	... Red heat	... about 90 per cent. of that required to form Fe_2O_3.	
,,	85 to 89.	100	,,	,,	.. Bright red ...	about 67·0	do.
,,	79	47	,,	,,	... Full red ...	8·2	do.
,,	80	11	,,	,,	Approaching whiteness.	11·9	do.
,,	92 to 94.	Nil.	,,	,,	... Bright red ...	1·	do.

The following trials show that the same variation in susceptibility of reduction in Fe_2O_3, having different molecular structure, is apparent when using a mixture of CO and CO_2, as was noticed in their treatment with pure CO.

A mixture of 100 vol. CO, and 50 CO_2, was prepared and exposed to the following substances in the lead bath:—

	Substance used.	Temp.	Hours exposed.	Oxygen per 100 Fe. Lost.	Residual.
Exp. 95.	Cal. Cleveland ore ...	Melting zinc. 417°C. 782°F.	5½ ...	·9	41·9
„ 96.	Fe_2O_3 from nitrate...		„ ...	2·4	40·4
„ 97.	Precip. Fe_2O_3		„ ...	2·9	39·9
„ 98.	Fe_2O_3 from cal. $FeSO_4$		„ ...	3·4	39·4
„ 99.	Cal. Cleveland ore ...		11½ ...	4·3	38·5
„ 100.	Precip. Fe_2O_3... ...		„ ...	14·0	28·8
„ 101.	Fe_2O_3 from nitrate ...		„ ...	16·2	26·6
„ 102.	Cal. Cleveland ore ...	Low red.	6 ...	5·8	37·0
„ 103.	Precip. Fe_2O_3		„ ...	19·6	23·2

With the two gases in the proportions of 100 CO to 31 CO_2, the following was the loss of oxygen:—

	Substance.	Temp.		Hours exposed.	Oxygen per 100 Fe Lost.	Residual
Ex. 104.	Cal. Clev. Ore	Melt. zc. 417°C.		5 ...	1·9	40·9
„ 105.	Precip. Fe_2O_3		Expos. in	„ ...	26·6	16·2
„ 106.	Cal. Clev. Ore		Lead bath	10½ ...	2·9	39·9
„ 107.	Do.	Low red.		5 ...	29·3	13·5
„ 108.	Precip. Fe_2O_3			„ ...	38·6	4·2

The results just given point very strongly to the conclusion that as soon as carbonic oxide has reduced oxide of iron to such an extent, that, for every 100 volumes of it in the altered gases, there exist about 50 volumes of carbonic acid, all further action on calcined Cleveland ore practically ceases at the temperature of melting zinc, and that it is very languid at something above 31 volumes of CO_2 to 100 of CO.

Now, an average temperature of melting zinc is above that of the escaping gases of the blast furnaces of the Cleveland district, where they have a capacity of about 12,000 cubic feet and upwards. From these, carbonic oxide and carbonic acid are given off in the proportions of about 75 of the former to 25 of the latter, which is that which, under the circumstances of temperature, may be considered as the point of static equilibrium; *i.e.*, such a mixture is unable to effect any appreciable reduction in Cleveland ore, at the same time there is no reason for supposing, but quite the contrary, that a gas which is practically inert on this ore may not be very active on peroxide of iron in another form. In proof of this, it will be observed that while calcined Clevel-nd

ore, in experiments 104 and 105, lost only 1·9 per cent. of its oxygen, precipitated $Fe^2 O_3$ had parted with 26·6 per cent.

SECTION IX.—ACTION OF GASES OF BLAST FURNACE ON OXIDE OF IRON.

The conditions of the experiments just enumerated, performed to determine the temperatures at which mixtures of CO and CO_2 commence to act on oxide of iron, were, however, not similar to those which obtained in the observations of M. Tunner and M. Ebelmen, made on the actual gases of the blast furnace. These gases consist of the two oxides of carbon, diluted with about double their united volume of nitrogen.

According to the former authority, a mixture of about 100 vol. CO, 125 vol. CO_2, and 540 vol. N, effected no change on the ore exposed to it in one hour, with the temperature gradually rising to 640°C. (1,180°F.), while M. Ebelmen mentions that about 100 vol. CO, 62 vol. CO_2, and 260 vol. N, produced no effect on ores of iron during two hours, with the temperature gradually increasing, but not reaching to that of redness.

From what has preceded it may be assumed as proved, that while there is a point, at certain temperatures where a quantity of CO_2 can arrest reduction beyond a certain extent, there is no quantity of this acid, which at others, can prevent a commencement of the process of deoxidation. In support of this, we have seen in experiment 82 a mixture of 100 vol. CO and 600 vol. CO_2 remove 5·8 per cent. of the original oxygen contained in Cleveland calcined ore in half an hour at a low red heat; and, again, a mixture of these two gases was (Ex. 81) entirely converted into CO_2 at something under a red heat.

The ores which were employed by M. M. Tunner and Ebelmen no doubt, were different from those used in the two last-mentioned experiments, but this could not affect the argument when applied to Cleveland stone, because, on referring to the various trials on different ores, it will be seen, of all those quoted, that the ironstone of the Cleveland hills appeared to retain its oxygen with the greatest tenacity.

Whatever importance may attach to the knowledge gained by a study of the action of mixtures of pure CO and CO_2 on oxides of

iron, for information of real practical value, we must have recourse to the diluted condition in which these two substances are found to exist in the blast furnaces themselves. Here, it is true, a difficulty arises from which the first-named research is almost exempt. In the latter, the relation between the CO and CO_2 can be maintained of uniform character, and the variation in the temperature is of a trifling nature. At the furnace, on the contrary, both these important conditions are liable to considerable fluctuation. The composition of the gas varies greatly as we shall see hereafter, and this is no doubt due to a change in the character of the chemical action going on at the period it quits the furnace, and the temperature is altered by the periodical introduction of cooler materials at the throat.

To satisfy myself of the general nature of the effect upon ores of iron by gas of different composition and different temperatures, as the same is emitted by furnaces varying considerably in size,* lengthened investigation was had recourse to, the results of which will be given under the heads of furnaces of 6,000, 11,600, 15,400, 25,500, 16,000, and 33,000 cubic feet, all smelting Cleveland ironstone.

FURNACE OF 6,000 CUBIC FEET. No. 4, AT CLARENCE WORKS.

Average temperature of escaping gases, 450°C., or 842°F.

EXPERIMENT 109.

Working calcined limestone.

Maxm. CO_2 observed per 100 vols. CO,	20 ...	Diluted with	218 N.
Minm. „ „ „	16 ...	„	166 N.
Average „ (1 day, 6 trials)	18 ...	„	184 N.

EXPERIMENT 110.

Working Raw limestone.

Maxm. CO_2 per 100 vols CO	26 ...	Diluted with	190 N.
Minm. „ „ „	23 ...	„	210 N.
Average „ (1 day, 4 trials.) ...	24·5	„	194 N.

EXPERIMENT 111.

Working raw limestone.

Maxm. CO_2 per 100 vols. CO... ...	18 ...	Diluted with	182 N.
Minm. „ „ „	15 ...	„	176 N.
Average „ (1 day, 5 trials.) ...	17 ...	„	178 N.
Average CO_2 from previous 15 trials	20 ...	„	185 N.

* The cause of these differences of composition and of temperature will be alluded o hereafter.

But the following experiments were all made while the furnace was using calcined limestone.

	Bi.	Pb.	Zn.	Sb.	Temp. about.	Time exposed.	Oxy. removed, that contained in Fe_2O_3=100.
Exp. 112. Cal. Clev. ore..	Melted	Softened	...	...	295°C=563°F	1 hour	7·7
Exp. 113. Cal. Clev. ore..	,,	Melted	...	...	330 626	2 ,,	11·8
Exp. 114. Cal. Clev. ore..	,,	,,	...	...	330 626	3 ,,	6·1
Exp. 115. Cal. Clev. ore..	,,	,,	Melted	...	420 788	6 ,,	54·3
Exp. 116. Cal. Clev. ore..	,,	,,	,,	Melted	450 842	12 ,,	55·4
Exp. 117. Cal. Clev. ore..	,,	,,	,,	Softened	425 797	18 ,,	61·9
Exp. 118. Cal. Clev. ore..	Not recorded.					24 ,,	close on 100.

This last experiment, however, appears to have been altogether an exceptional case. Another trial, under the same conditions as to temperature, gave only 62 per cent. of removed oxygen. in 24 hours; whilst in another experiment, when the temperature was not quite so high (lead melted), only 38 per cent. of the O was lost; and in another instance, only 24 per cent. was thus removed in 24 hours. In experiment 118, there is no doubt, probably from a temporary great diminution in the quantity of CO_2 in the gases, a considerable amount of iron was reduced to the state of metal, because the residue, on being treated with H Cl, afforded a gas which was almost pure hydrogen.

The specimens of ore were placed on a flat iron tray, and exposed to the direct action of the gases; but in the following four trials, the ore was contained in an iron box, open at the top, with perforated sides, and therefore approaching to the condition of the apparatus used by M. Ebelmen and M. Tunner.

Substance used.	Bi.	Pb.	Zn.	Sb.	Temp. about.	Time exposed.	Oxy. removed, that contained in Fe_2O_3=100.
Exp. 119. Cal. Clev. ore..	Melted	Melted	Melted	Softened	425°C=797°F	24 hours	41
Exp. 120. Cal. Clev. ore..	,,	,,	,,	,,	420 788	48 ,,	52
Exp. 121. Cal. Clev. ore..	,,	,,	,,	Melted	430 806	72 ,,	59
Exp. 122. Cal. Clev. ore..	,,	,,	,,	,,	430 806	96 ,,	61

In these it will be observed that the protection which the shelter afforded by the sides of the box* has materially interfered with the rate of deoxidation. This circumstance leads me to infer that the apparatus employed by these gentlemen, more liable from the nature of its construction to this objection, has caused the great difference between their results and my own.

The method pursued for estimating the loss of oxygen in the trials just recorded consisted in ascertaining, by means of a permanganate solution of known strength, the amount of iron in the ore previous and subsequent to exposure to the furnace gas, and from this the loss of weight was estimated, the dust which adhered to the specimens during the operation preventing the difference being ascertained by direct weighing. It must be observed that the figures represent a loss of oxygen somewhat under the truth, in consequence of an increase of weight arising from a cause which will be considered immediately.

FURNACE OF 11,600 CUBIC FEET. No. 2, AT CLARENCE WORKS.

Average temperature of escaping gases, 321°C., or 610°F.

Ex. 123.	Maximum	CO_2	observed	per 100 vol.	CO...	50	vol.	CO_2	... diluted with	350 N.
,, 124.	Minimum	,,	,,	,,	...	32	,,	...	,,	187 N.
,, 125.	Average	,,	one day	,,	8 trials...	44	,,	...	,,	239 N.
,, 126.	Do.	,,	,,	,,	6 ,, ...	39	,,	...	,,	205 N.

Substance used.	Bi.	Pb.	Zn.	Sb.	Temp. about.	Time exposed.	O removed, that contained in Fe_2O_3=100.
Exp. 127. Cal. Clev. ore	Melted	...	...	...	270°C=517°F	1 hour	4·20
Exp. 128. Cal. Clev. ore	,,	Softened	...	...	295 563	2 ,,	4·75
Exp. 129. Cal. Clev. ore	not recorded.		...	...	...	24 ,,	53·64
Exp. 130. Weilburg red ore Fe_2O_3	Do.		...	...	...	7½ ,,	11·99
Exp. 131. Wetzler brown Fe_2O_3	Do.		...	...	...	7½ ,,	16·88

FURNACE OF 25,400 CUBIC FEET. No. 6, AT CLARENCE WORKS.

Average temperature, 312°C., or 594°F.

Exp. 132.	Maximum	CO_2	observed	per 100 vol.	CO...	45	vol.	CO_2	... diluted with	192 N.
,, 133.	Minimum	,,	,,	,,	...	34	,,	...	,,	191 N.
,, 134.	Average	,,	one day	,,	7 trials...	40	,,	...	,,	204 N.
,, 135.	Do	,,	,,	,,	6 ,, ...	35	,,	...	,,	189 N.

* In the estimates of temperature the fusing points are taken as for Bi 264°C. or 507°F., Pb 327°C, or 620°F., Zn 417°C. or 782°F., Sb. 450°C. or 842°F.

Substance used.	Bi.	Pb.	Zn.	Sb.	Temp. about.	Exposed.	Loss of original O per cent.
Exp. 136.							
Cal. Clev. ore..	Melted.	Softened	...	...	295°C=563°F	1 hour	5·31
Exp. 137.							
Cal. Clev. ore..	,,	,,	...	...	295 563	2 ,,	6·10
Exp. 138.							
Cal. Clev. ore..	,,	,,	...	...	270 517	24 ,,	3·72
Exp. 139.							
Cal. Clev. ore..	,,	,,	...	...	295 563	48 ,,	5·71
Exp. 140.							
Cal. Clev. ore...	,,	,,	...	...	295 563	72 ,,	27·82
Exp. 141.							
Cal. Clev. ore...	,,	,,	...	...	430 806	96 ,,	28·30

In the case of four experiments (Nos. 138 to 141), the samples were enclosed in the box with perforated sides, and the same effect is perceptible here as happened in the furnace of 6,000 cubic feet, viz., a great retardation in the process of reduction; an exposure of 24 hours in the box having removed less oxygen than that of one hour in the open tray.

FURNACE OF 16,000 CUBIC FEET. No. 4, AT FERRYHILL.

Average temperature of escaping gases, 199°C., or 390°F.

Exp. 142.	Maximum of CO_2 per 100 vol. CO	... 46 vol CO_2	... diluted with	202 N.
,, 143.	Maximum ,, ,,	... 36 ,,	... ,,	200 N.
,, 144.	Average of 1 day. 5 trials ,,	... 40 ,,	... ,.	205 N.

	Substance used.	Temperature.	Exposed.	Loss of original O.
Exp. 145.	Cleveland calcined ore...		55 hours ...	17·4 per cent.
,, 146.	Rosedale calcined ore, also Oolitic, but from another bed, and containing 48 per cent of Fe	Maximum not observed ...	55 ,, ...	16·9 ,,

FURNACE OF 33,000 CUBIC FEET. No. 9, AT FERRYHILL.

Average temperature of escaping gas, 194°C., or 381°F.

Exp. 147.	Maximum of CO_2 per 100 vol. CO	... 43 vol. CO_2	... diluted with	222 N.
,, 148.	Minimum ,, ... ,,	... 30 ,,	... ,,	206 N.
,, 149.	Average of 1 day. 5 trials ,,	... 36 ,,	... ,,	218 N.
,, 150.	Do 4 ,, ,,	... 33 ,,	... ,,	199 N.

	Substance used.	Temperature.	Hours.	Original O removed.
Exp. 151.	Cleveland calcd. ore ...	Max. temp.	55	8·0 per cent.
,, 152.	Rosedale calcd. ore	not observed	55	6·0 ,,

It is necessary to state that the temperatures quoted as those at which the gases leave the furnace at Ferryhill, as well as those to which the various specimens of ores have been exposed, cannot be regarded as strictly correct. The observations from which the heat of the gases was deduced, were made by immersing therein,

for some minutes, a cylinder of copper of a given weight, and then plunging it into a known quantity of water. From the temperature acquired by this water the total quantity of heat absorbed by the copper was ascertained, and from it the sensible heat of the gases was estimated.

The objection to this apparatus is the difficulty of always obtaining copper possessing precisely the same specific heat. The gradual though imperceptible loss of weight, particularly at high temperature, of the cylinder also affects the result. Again, the mass of copper needs a certain time before it acquires the heat of that of the medium by which it is surrounded, and the temperature of the gases being a constantly changing one, the cylinder can never be said to be exactly as hot as the gases at the moment of its being withdrawn.

Besides the apparatus just described, a pyrometer, made by M. Kraus, was frequently employed. It consisted of a metallic spiral, enclosed in an iron tube, the expansion of which indicated the temperature. This has the same defect as the copper cylinder, viz., loss of time in acquiring the temperature of the gases. To avoid this, I had a copper tube made of as thin a substance as would bear the pressure the air within when heated would exercise on its sides. Connected with it was a mercurial gauge which showed the amount of compression the imprisoned air had experienced, and thus indicated the temperature. I found this very quick in its manifestations.

The figures given in this work, however, have the merit of being the result of a very great number of observations, extending at various periods over several consecutive hours, and at all events are, comparatively speaking, approximatively correct.

With regard to the heat to which the various samples of ore were subjected, as estimated by the fusion of different metals, this, of course, also was only approximative, inasmuch as when one metal melted, and the next above it was not affected, the temperature could not be exactly ascertained, by as much as the fusing point of the one differed from that of the other. Thus, when bismuth melted and lead was not affected, there was an unknown margin of 327° to 264°, or 63°C. (113°F.) This inconvenience might have been avoided by the use of the alloys employed by M. Tunner, but even then a mere approach to correctness would have been reached, for

the pieces of test metal became coated with the fine dust or sublimate after a few hours sojourn in the gases which protected them from being immediately affected by changes of temperature. In this way I account for the fact that, although the average temperature of the escaping gases of the Clarence furnace No. 4 was a few degrees above that of melting antimony, this metal was not always fused in the trials, even when they extended over some hours.

It must also be remembered that the circumstance of a metal having been fused, is merely indicative of the maximum temperature to which the escaping gases have reached, and not of the average. Upon each occasion of materials being introduced, the heat of the gases falls, and when charging for any reason is discontinued their temperature rises steadily. As illustrating the nature of these fluctuations, the following is a record of the variations observed upon one occasion, the readings being taken five minutes before and after each charge.

	Temperature before charging.		Charge.		Temperature after charging.	
Exp. 153.	655°F=346°C....		24 cwt. coke ...		640°F.=338°C.	
	525	274 ...	50 „ mine & flux		495	256
	495	256 ...	24 „ coke ...		450	232
	435	224 ...	50 „ mine & flux		415	213
	420	215 ...	24 „ coke ...		400	204
	380	193 ...	50 „ mine & flux		365	185
	475	246 ...	24 „ coke ...		430	221
	405	207 ...	50 „ mine & flux		405	207
	395	202 ...	24 „ coke ...		375	191
	370	188 ...	50 „ mine & flux		365	185
	Furnace full.		Ceased charging for one hour.			
	700	371 ...	24 cwt. coke ...		625	329
		Furnace nearly four feet down.				
	565	296 ...	50 cwt. mine & flux		535	268
	530	276 ...	24 „ coke ...		510	264
	460	238 ...	50 „ mine & flux		445	229

In this case the coke ovens and calcining kilns were both at the furnace, hence, occasionally, all the materials were somewhat warm.

The following is the record of the temperature of the escaping gases at one of the Clarence furnaces, extending over a little above

three hours, during part of which no materials were introduced, in order to ascertain the rate of increase in temperature:—

	Hour.		Temperature.	
Exp. 154.	10	5 a.m.	575°F.	=302°C.
	„	10	605	318
	„	15	670	354
	„	20	700	371
	„	25	750	399
	„	30	800	427
	„	35	835	446
	„	40	875	468
	„	45	935	502
	„	50	975	524
	„	55	1015	546
	11	0	1025	552

Furnace three rounds down, or twelve complete charges of coke, mine, and flux.

	11	5	1075	579
	„	10	1140	615
		Put on coke, 25 cwts.		
	„	15	1140	615
		Put on mine and flux, 65½ cwts.		
	„	20	1025	552
	„	25	930	499
	„	30	930	499
		Put on coke, 25 cwts.		
	„	35	930	499
		Put on mine and flux, 65½ cwts.		
	„	40	930	499
		Put on coke, 25 cwts.		
	„	45	800	427
	„	50 Put on mine and flux, 65½ cwts.		
	„	55	750	399
		Put on coke, 25 cwts.		
	12	0	725	385
	„	5 Put on mine and flux, 65½ cwts.		
	„	10	680	360
	1	10	1070	577

In this instance, the temperature of the gases has, from the mode of charging pursued, run up considerably above the average of that at which they usually left this furnace, which does not generally exceed 630°F. (332°C.)

All this heat, however, is not the result of the oxidation of the fuel. The ironstone is calcined on the works, and frequently has a temperature considerably above 100°C. (212°F.) When all the materials are supplied into a furnace of its size (11.500 cubic feet) at the temperature of the atmosphere, the gases escape at about 210°C. (410°F.), or 122°C. (220°F.) below that at which they do when using hot ironstone.

The gaseous contents of a blast furnace rushing through the solid materials are endowed with two properties. In the first place, the power of raising the temperature of the substances they meet on their way to the summit by virtue of the sensible heat they contain; and, secondly, the faculty of reducing oxide of iron by reason of the carbonic oxide which enters largely into their composition.

It is manifest that if the gases in question are permitted to leave the furnace before they have parted with as much of their sensible heat as circumstances will permit, or escape before they have become charged with as much oxygen derived from the ore as they are capable of holding, a corresponding loss must be an inevitable consequence.

The temperature and the composition of the gases from furnaces of different dimensions have been given here at some little length, but the subject will demand still further attention when the question of capacity comes up for consideration. In the meantime, it may be observed from the information afforded by experiments, that when the gases from a blast furnace escape at a temperature of about 420°C. (788°F.), and are charged with as much oxygen as will give a composition of 20 vols. of CO_2 for 100 vols. of CO, they were found capable of removing 8·31 per cent. of the original oxygen in a specimen of Cleveland ore per hour. On the other hand, when from a change in the character of the furnace this temperature was lowered to 295°C. (563°F.), and the proportions of CO_2 to CO were as 40 to 100, then the power of the gases as they quitted the furnace possessed little above one-fourth of the reducing power given above, *i.e.*, only 2·37 per cent. of the original oxygen was removed instead of 8·31.

It must further be remarked that any two numbers do not necessarily express correctly the comparative deoxidizing power of a mixture, because it is an ascertained fact, that the first portions of oxygen in an oxide of iron are much more easily expelled, than those which are removed subsequently.

Exp. 155. The following figures represent, at a temperature varying from 215° to 225°C. (419° to 437°F.), the gradual decrease in the rate of deoxidation extending over 16 hours:—

1st hour.	Loss of O, assumed as unity ...	1·00	per hour.
2nd & 3rd	„	·70	„
7th	„	·58	„
8th	„	·58	„
9th	„	·52	„
10th	„	·52	„
12th	„	·50	„
13th & 14th	„	·50	„
15th & 16th	„	·42	„

At the end of the sixteenth hour, almost one-fourth of the original oxygen had been removed. Whatever objection may be raised to the results given in these pages, on the score of deviation from perfect truth in any particular case, there runs through the whole that uniformity which might, under the circumstances, be expected, viz., an augmenting rate of deoxidation as the gases rise in temperature, and as they increase in the proportion they hold of the reducing agent, CO. Further, they teach us that instead of a temperature of 650°C. (1,202°F.), being required for reduction, 200°C. (392°F.) is sufficient—a temperature, which, in the case of the smaller fragments of ore, will, it is obvious, be attained in a very few minutes after their introduction into a blast furnace.

No doubt, according to the analyses contained in M. Tunner's paper, the gases of the Austrian furnaces are loaded to an extraordinary extent with CO_2, but, inasmuch as it was proved in experiment 82, that at a low red heat Cleveland ore lost in half an hour in a mixture of 100 vols. of CO to 600 of CO_2 5·8 per cent. of its oxygen, it is difficult to understand how gases, consisting of 100 of CO to 120 or 130 of CO_2, even when largely diluted with N, should be inert at a temperature of above 620°C, (1,148F.), and this upon an ore more susceptible of reduction than that just mentioned.

SECTION X.—REDUCING EFFECTS OF GASES AT DIFFERENT DEPTHS OF THE BLAST FURNACE.

Having thus satisfied myself of the nature of the action of gases as they flow from the top of furnaces of different sizes, and which, in consequence of altered capacity, vary in composition and temperature within the limits already described, I proceeded to examine their effect as a reducing medium at the higher temperatures which prevail at greater depths in the furnace. With this view, in order to avoid the objections I conceived attended the method pursued by M. Tunner and M. Ebelmen, the sides of the furnaces were bored at different heights, and when it was desired to ascertain the action of the hot gases at any particular point, samples of ironstone in pieces, about the size of hazel nuts, were placed near the end of a porcelain tube, and this extremity thrust through the hole a little way into the contents of the furnace, so as to expose the ore to the influence of the gases, as nearly as might be, at the temperature at which they were passing up the interior of the furnace. This was effected by a rapid current being forced along the tube by the state of compression in which the gases are always found during their ascent among the materials under treatment.

In the following experiments the composition of the gases is given according to determinations by several analyses made on different occasions, and the extent of oxygen removed was estimated by the method previously described, viz., determination of the quantity of that element which was required to reconvert the partially reduced ore to Fe_2O_3.

The first series of experiments was made upon the furnace No. 4, at the Clarence Works, containing 6,000 cubic feet.

At a perforation in its side 4 feet 3 inches from top of furnace.

Temperature, no signs of redness.

Composition of gases on four different days:—*

Exp. 156.	100 vol. CO	...	19 vol. CO_2	...	187 vol. N.	...Working calcd. limestone.		
,, 157.	100 ,,	...	28 ,,	...	181 ,,	...Working raw	do.	
,, 158.	100 ,,	...	21 ,,	...	187 ,,	...Working calcd.	do.	
,, 159.	100 ,,	...	23 ,,	...	200 ,,	...Working raw	do.	
,, 160.	Calcd. Clev. ore, exposed for two hours.					Loss of original O ... 13·7 per cent.		
,, 161.	Do.	do.	Second trial.			do.	10·04	,,

* Fractions omitted.

At a perforation in side 9 feet 9 inches from top of furnace. Temperature, cherry red.

Composition of gases on four different days :—

Exp. 162.	100 vol. CO	...	6 vol. CO_2	...	106 vol. N.	...Working calcd. limestone.
,, 163.	100 ,,	...	5 ,,	...	169 ,,	...Working raw do.
,, 164.	100 ,,	...	6 ,,	...	159 ,,	...Working calcd. do.
,, 165.	100 ,,	...	12 ,,	...	176 ,,	...Working raw do.
,, 166.	Calcd. Clev. ore, exposed for two hours.					Loss of original O ... 76·2 per cent.

At a perforation in side 15 feet 7 inches from top of furnace. Temperature, bright red.

Composition of gases on four different occasions :—

Exp. 167.	100 vol. CO	...	1 vol. CO_2	...	180 vol N.	...Working calcd. limestone.
,, 168.	100 ,,	...	6 ,,	...	177 ,,	...Working raw do.
,, 169.	100 ,,	...	1 ,,	...	165 ,,	...Working calcd. do.
,, 170.	100 ,,	...	1 ,,	...	162 ,,	...Working raw do.
,, 171.	Clev. calcd. ore, exposed for two hours.					Loss of original O ... 76·3 per cent.
,, 172.	Do.	do.	upon another occasion			71·26 ,,

At a perforation in side 21 feet 5 inches from top of furnace· Temperature, very bright red.

Composition of gases on three different days :—

Exp. 173.	100 vol. CO	...	1 vol. CO_2	...	170 vol. N.	...Working calcd. limestone.
,, 174.	100 ,,	...	Nil.	...	185 ,,	...Working raw do.
,, 175.	100 ,,	...	7 vol. CO_2	...	180 ,,	...Working calcd. do.
,, 176.	100 ,,	...	6 ,,	...	182 ,,	...Working raw do.
,, 177.	Clev. calcd. ore, exposed for two hours.					Loss of original O ... 68·2 per cent.
,, 178.	Do.	do.	upon another occasion			81·76 ,,

At a perforation in side 27 feet 3 inches from top of furnace. Temperature, very bright red.

Composition of gases on four different occasions :—

Exp. 179.	100 vol. CO	...	5 vol. CO_2	...	170 vol. N.	...Working calcd. limestone.
,, 180.	100 ,,	...	4 ,,	...	177 ,,	...Working raw do.
,, 181.	100 ,,	...	7 ,,	...	179 ,,	...Working calcd. do.
,, 182.	100 ,,	...	6 ,,	...	168 ,,	...Working raw do.
,, 183.	Clev. calcd. ore, exposed for two hours.					Loss of original O ... 68·1 per cent.
,, 184.	Do.	do.	upon another occasion			73·83 ,,

The following experiments were performed at the Wear furnace, having a cubic capacity of about 17,500 feet.

At a perforation in side 25 feet 11 inches from top of furnace. Temperature, bright red—gave by copper cylinder 860°C. 1,580°F.

Composition of gases on three different occasions —

Exp. 185.	100 vol. CO	...	4 vol. CO_2	...	194 vol. N.	...Working calcd, limestone.
,, 186.	100 ,,	...	7 ,,	...	182 ,,	... ,, ,,
,, 187.	100 ,,	...	9 ,,	...	203 ,,	...Working raw do.
,, 188.	Clev. calcd. ore, exposed for two hours.					Loss of original O ... 84·6 per cent.

At perforation 52 feet from top of furnace. Temperature, very bright red. Copper melting (1000° to 1200°F.)

Composition of gas upon three different occasions.

Exp. 189.	100 vol. CO	...	2 vol. CO_2	...	177 vol. N.	...Working calcd. limestone.
,, 190.	100 ,,	...	2 ,,	...	170 ,,	... ,, ,,
,, 191.	100 ,,	...	3 ,,	...	182 ,,	...Working raw do.
,, 192.	Calcd. Clev. ore, exposed two hours. Loss of original O ... 81·0 per cent.					

At perforation 70 feet 4 inches from top of furnace. Temperature, higher than last experiment.

Composition of gas on three different occasions:—

Exp. 193.	100 vol. CO	...	0 vol. CO_2	...	183 vol. N.	...Working calcd. limestone.
,, 194.	100 ,,	...	0 ,,	...	200 ,,	... ,, ,,
,, 195.	100 ,,	...	0 ,,	...	190 ,,	...Working raw do.
,, 196.	Clev. calcd. ore, exposed for two hours; but a part of this time the tube was closed, and no gas was passing through. Loss of O, 81·8 per cent.					

It has already been suggested that possibly a form of apparatus which would impede the free current of the reducing gases, might interfere with the results. This, I conceive, would arise from the current, thus retarded in its passage through the perforated box, gradually becoming richer in CO_2 than that of the general volume in the furnace itself. It is true the proportion of CO_2 given as existing in the furnaces at particular points, and upon which the conclusions of Messrs. Tunner and Ebelmen were based, greatly exceeded that which, in the Clarence and Wear furnaces, produced the effects just quoted. But, on the other hand, it will be remembered that a mixture of 100 vol. CO, 125 vol. CO_2, and 546 vol. N, in experiment 81, at a temperature a little above melting zinc (probably about 430°C.) when passed over calcined Cleveland ore, has, practically, been entirely converted into CO_2, and that the ore lost above 5 per cent. of its original oxygen in $1\frac{3}{4}$ hours. This composition of gas was purposely adopted as being that of the Wrbna furnace, examined by M. Tunner, in which, at a temperature of near 600°, is returned as being without any action on ores, certainly more susceptible of deoxidation by CO than that employed in my own experiments.

The ores of La Chapelle and Laissey, examined by M. Ebelmen, contained, it is true, from 4 to 5 per cent. of water, but after this was entirely expelled, and the gases all but free from any CO_2 whatever, with a bright red heat, the rate of reduction proceeded according to the account he gives, far below that at which, I conceive, a furnace is capable of effecting deoxidation.

SECTION XI.—DISSOCIATION OF CARBONIC OXIDE IN THE BLAST FURNACE.

In the reduction of an oxide of iron to the metallic state by CO, so far as I know, the accompanying chemical action has been hitherto considered as the direct and entire conversion of this oxide of carbon into CO_2. Sufficient reasons have been given to shew that an excess of CO is always required to effect complete deoxidation, so that the formula, representing the change which occurs, may be taken as—

$$Fe_2O_3+(x+3)\ CO=2\ Fe+3\ CO_2+x\ CO.$$

the value of x CO, possibly varying with the character of the ore, or oxide, under treatment.

Although the equation just mentioned may, and does correctly express final results attending the reduction of peroxide of iron, I will now endeavour to prove that it is highly probable these are obtained by the exercise of an action of an intermediate nature.

Some time ago, after exposing samples of ores to the escaping gases of different blast furnaces, I observed that the substances operated upon afforded, on being dissolved in HCl, a black residuum varying in intensity of colour according to the temperature and richness in CO of the gas in which they had been immersed. The residue in question was the portion of the ore insoluble in the acid, and the blackness, I ascertained, was due to carbon in a finely divided state.

The circumstance was communicated to the Chemical Society of London,* and subsequent investigation satisfied me it was owing to an actual decomposition of the carbonic oxide, contained in the escaping gases, this body being resolved into carbon and carbonic acid by the action.

$$2\ CO=C+CO_2:$$

The experiment demonstrating this, was described in a paper read before the Chemical Section of the British Association, at its Exeter meeting.†

* *Vide* "Transactions of Chemical Society, May, 1869.

† *Vide* "Transactions of British Association for Advancement of Science," 1869.

Previous writers had, in general terms, mentioned that, at high temperatures, *reduced iron* acquired carbon during its passage through the furnace, and M. C. Schinz, I afterwards found, describes certain experiments,* in which, he, by exposing pure oxide of iron, and some ores, at a temperature of 800° to 900°C. (1,432° to 1,652°F.) to an atmosphere of carbonic oxide, mixed with twice its volume of nitrogen, had obtained minute quantities of carbon, after an exposure of from six to nine hours, the appearance of which, he considered, dependent on the previous production of metallic iron.

I only recently learnt that M. Caron had shown that oxide of iron, when exposed to a current of CO, at something under a red heat, became charged with carbon in considerable quantities. I am not aware of the extent to which this chemist has pushed his enquiries on this reaction, which has not hitherto been looked upon as playing, what I believe to be, an indispensable part in the smelting of iron—so much so, indeed, that there exists good grounds for believing that iron ores, in the blast furnace, are never brought to the metallic state by the direct action of CO in the way hitherto supposed.

The reasons upon which this view rests, will be best developed by a description of the conditions requisite for this splitting up of carbonic oxide giving rise to this deposition of carbon, which I have described as a process of carbon impregnation, in a paper read before the members of the Iron and Steel Institute.†

In this description I shall follow the order observed in considering the reduction of the oxide of iron, viz.:—first, the influence of temperature; and second, the manner in which the action is affected by the presence of carbonic acid, to which will be added the behaviour of oxide of iron and metallic iron while CO in their presence is split up into C and CO_2.

All previous researches appeared to indicate that a pretty high temperature was requisite for the process in question, apparently not under 500° to 600°C. (932° to 1112°F.). My own experiments on the blast furnace gases proved that, in all probability, a little above 300C. (572°F.) produced the change, and that with pure CO 200°C. (392°F.) sufficed.

The apparatus employed for ascertaining whether even a lower

* Dokumente betreffend den Hohofen.

† *Vide* "Transactions of Iron and Steel Institute."

degree of heat than this was not sufficient to decompose the CO by an iron oxide, was that described in experiments 13 to 18, for determining the temperature at which deoxidation of this compound commences, viz., the Liebig's drying tube, immersed in an air bath.

It will be remembered, the precise moment of the first appearance of deoxidation could be noted by the indication of the presence of CO_2, manifested by rendering lime water turbid. This mode, however, could not be adopted in treating an oxide of iron to learn the first signs of carbon deposition, because of the previous formation of CO_2 produced by deoxidizing the iron oxide under examination.

At low temperatures the decomposition of CO proceeds at a very slow rate; consequently, for any marked manifestations of the carbon deposition, the operation must be continued for some time, particularly in the case of certain ores. The temperatures, which will be given presently, must not, therefore, necessarily be considered as the very lowest at which the decomposition is possible.

Exp. 197. A portion of anhydrous precipitated Fe_2O_3 was maintained at a temperature which fluctuated between 243° and 265°C. (469 to 509°F.). For two hours a current of CO, dried and purified in the manner previously observed, was passed over the heated oxide, after which, the apparatus was allowed to cool, the current of CO being continued until cold. The oxide was dissolved in H Cl, and the residual carbon collected, and found to weigh 1·28 per cent. calculated upon the iron contained in the residue.

Exp. 198. The same oxide of iron was similarly treated as in the previous experiment, but the temperature employed was 232° to 254° C. (449° to 489° F.), and the operation was continued for 6 hours. At the end of this time, the deposited carbon was found to be equal to 4·67 per cent. of the Fe contained in the oxide used.

The two following experiments were performed to compare the power of Cleveland ore to absorb carbon, with that of pure oxide of iron :—

Calcd. Clev. Ore.	Temperature.	Time of exposure.	Carbon deposited per 100 Fe in ore.
Exp. 199.	210° to 277° C. (410° to 530° F.)	... 1⅓ hours.	nil.
„ 200.	213° „ 221° C. (415 „ 430° F.)	... 20½ „	1·85

In the case of the Cleveland ore, the carbon was, of course, mixed with the silica, &c., insoluble in the H Cl used for removing the iron,

so that mere weighing, as in the case of the pure oxide, was no longer admissible. The insoluble substance, therefore, was collected on a filter of asbestos, properly washed and dried, and then placed in a combustion tube. The tube, being heated to redness, had pure oxygen conducted through it, and the resulting gas passed then through heated cupric oxide to ensure its entire conversion into CO_2, it being found that very considerable quantities of CO were produced when this precaution was neglected. The usual methods of drying the CO_2, &c., being observed, this gas was collected in bulbs, containing KHO, weighed, and from it the C was calculated. In some instances, the insoluble portion, containing carbon, was burnt, together with the asbestos filter with chromate of lead, and the CO_2 produced collected as before.

On referring to the experiments 17 and 18, it will be perceived that at 205° to 210° C. (401° to 410° F.), the deoxidation of Cleveland calcined ore had just fairly set in. In that numbered 200, just mentioned, carbon impregnation, after 20½ hours, was clearly effected. In the experiment which immediately precedes it, the average temperature was somewhat higher, without any carbon being deposited, but then the time was much shorter, 1½ hours, instead of 20½ hours, and it may be remarked in the former, deoxidation had barely set in, only ·47 per cent. of the original O being removed. On the whole, it seems highly probable that the carbon impregnation by the splitting up of CO takes place at as low a temperature as deoxidation, which, in the case of Cleveland calcined ore, is at 200° to 210° C. (392° to 410°F.)

Experiment 26, and others which immediately follow it, demonstrated in how marked a manner the extent of reduction was affected by peculiarities of the ore or oxide of iron when submitted under perfectly similar circumstances to the action of CO. In the absence of all other apparent cause in the case of artificially prepared and chemically pure oxides, this difference of behaviour was, in them, ascribed to mere differences in molecular condition. By inference, the same cause was considered to hold good with ores of various kinds. Whether this explanation be correct or not, the same irregularity in the extent to which carbon impregnation takes place in different substances, has been found to obtain as that observed in deoxidation; and, moreover, generally speaking, the more readily does an ore or oxide of iron lose its oxygen, the more capable is it of precipitating carbon from CO.

To obtain more marked results, it was found better to apply a higher temperature than that hitherto mentioned in connection with this subject, the action being, as has been pointed out, a very slow one. A heat of melting zinc was aimed at, and to secure in all respects identity of treatment, six or seven specimens of different varieties were exposed simultaneously in the lead bath arrangement already described.

The following numbers were obtained after a seven hours' exposure, during which time the maximum temperature was that indicated by the fusion of zinc, while antimony was not affected, probably, therefore, 420°C. (788°F.) The amount of carbon, in all cases, being determined by combustion in oxygen, with the addition of the tube containing Cu O, so as to secure complete conversion of the C to CO_2:—

	Substance employed.	Carbon per 100 of substance.	Carbon per 100 Fe present.
Exp. 201.	Fe_2O_3 from the nitrate	56·3 ...	144·0
„ 202.	Precipitated Fe_2O_3	45·5 ...	95·4
„ 203.	Fe_2O_3 from calcined Fe SO ...	31·9 ...	54·5
„ 204.	„ on pumice-stone	1·69 ...	14·9
„ 205.	Calcined Cleveland ore	·11 ...	0·3

Along with these was also a specimen of precipitated Fe_2O_3 which had been previously exposed to the carbon depositing action.

Exp. 206. After the first exposure it contained 52·14 per cent. of C, equal to 148·4 per 100 Fe.

Exp. 207. After the second exposure it contained 64·4 per cent. of C, equal to 225·2 per 100 Fe.

The following numbers were obtained at a temperature slightly below that of the previous experiments, but in which the time of exposure was extended to nine hours in the lead bath.

Exp. 208. Pumice-stone, saturated with Fe_2O_3 from Fe SO_4, gave 770 of C per 100 of Fe.

Exp. 209. Precipitated anhydrous Fe_2O_3, gave 181 of C per 100 of Fe.

Exp. 210. Fe_2O_3 from calcined Fe SO_4, gave 142 of C per 100 of Fe.

In similarly conducted experiments, at a higher temperature, but not visibly red hot:—

Exp. 211. Calcined Cleveland ore, after 4½ hours' exposure, afforded 64·0 of C per 100 of Fe present.

Exp. 212. Calcined Cleveland ore, in a tube, after 12 hours' exposure, afforded 86·13 of C per 100 of Fe present.

In neither of these last two trials was the CO purified by nitrate of silver, so that it is just possible traces of hydrocyanic acid may have been present.

As examples of the superior power of other ores, compared with that of Cleveland, to become impregnated with this deposited carbon, may be quoted the following:—

Exp. 213. Lancashire hæmatite, containing 40·3 per cent. of Fe, temperature about 415°C. (779°F.), exposure 7½ hours, afforded 65·3 of carbon per 100 of Fe.

Upon another occasion, the two undermentioned specimens, exposed in the lead bath at the same time, afforded the annexed quantities of carbon:—

Exp. 214. Hæmatite, same as experiment 213, temperature, about 415°C. (779°F.), exposure 7½ hours, afforded 531·0 carbon per 100 Fe.

Exp. 215. Calcined Cleveland ore, exposed for 7½ hours, afforded 4·686 carbon per 100 Fe.

Exp. 214, may be quoted as an instance of the carbon precipitation being affected by apparently very insignificant differences of condition, for in it 531 per cent. of the weight of the iron present of carbon was obtained; whereas, in experiment 213, the same substance, Lancashire hæmatite, only 65·3 per cent. of carbon was obtained, although, to all appearances, the conditions as to heat and time of exposure were the same in each case.

In describing the circumstances which affected the rate at which oxygen was expelled from its compounds with iron by CO, allusion was made to the speed at which the gas was passed over the iron oxides. In experiments 34 to 39, reduction was performed by a slow current of CO, while, in those numbered 43 to 48, a rapid current of the gas was employed.

In the following trials, the same specimens from the sample were used, and each particular specimen occupied the same position in the lead bath apparatus, in both sets of experiments. The rate of carbon deposition is given to shew, that this phenomenon, like reduction, is influenced by the speed of the current of CO.

The exposure in each case was for 6 hours, at a temperature of 410°C. (770°F.) zinc softened.

CO used.		Slow current. 63 litres.		Rapid current. 245 litres.	
Calcd. Clev. ore, 40 pr ct. Fe	Ex. 216.	C per 100 Fe	12·6	Ex. 222.	C pr. 100 Fe 22·3
Lancashire ore 66·6 ,, ,,	,, 217.	do.	60·1	,, 223.	do. 270·8
Elber ore ..... 66·8 ,, ,,	,, 218.	do.	3·8	,, 224.	do. 4·9
Calcd. Spathose 51·7 ,, ,,	,, 219.	do.	2·3	,, 225.	do. 3·9
Fe_2O_3 precpd. 70 ,, ,,	,, 220.	do.	78·7	,, 226.	do. 335·4
do. calc. $FeSO_4$ 70 ,, ,,	,, 221.	do.	90·9	,, 227.	do. 476·5
Average			41·4	Average.....	185·6

In all probability, very small differences of temperature, however, are capable of greatly affecting the quantity of carbon yielded by the CO. In experiment 211, 100 of Fe in calcined Cleveland ore, at a temperature not visibly red, the carbon deposited in 4½ hours was 64·0. Using the same quality of ore, the following figures were obtained:—

		Carbon deposited.
Exp. 228.	Temperature, 11 hours red hot, for 10 hours bright red, in all 21 hours	2·3 per cent. of Fe.
,, 229.	Temperature, very bright red heat 4½ hours	0·3 ,,

Thus, practically, it may be assumed that the phenomenon of permanent carbon deposition diminishes very rapidly as soon as a red heat is reached, and that the temperature most favourable for its production is between 400 and 450°C. (752° and 842°F.)

Exp. 230. The same law holds good with pure oxide of iron, for when CO was passed over anhydrous precipitated Fe_2O_3 for five hours at a bright red heat it only contained, after the operation, ·25 per cent. of C reckoned on Fe in the residue.

Allusion has been made to the probability of molecular structure affecting the rapidity with which an ore or oxide of iron is capable of splitting up CO into C and CO_2. There seems good reason for assigning this as the cause why an oxide of iron prepared in one way is more active than one prepared in another, and why one ore should differ from another. Moreover, the marked irregularity in amount of C deposited which occasionally manifests itself in treating the same species of ore, dried perhaps in a slightly different way, and Fe_2O_3 prepared by the same process, calcined perhaps at a different temperature, seem to indicate that a slight change in the molecular state of the same substance may considerably affect its conduct, when placed under the influence of heated CO. Nay, indeed, a portion of the same precipitated Fe_2O_3 in fine powder, when exposed in a dish to the current of this gas, instead of being equally permeated by the carbon will, on its surface, have large

blotches of pure C, as if the action had been concentrated on points At other times the action is more uniform, and the powdered oxide forming a layer ·10 inch thick, will swell up to three or four times this depth.

When the oxide of iron under treatment is in the form of calcined iron ore no two fragments probably have exactly the same mechanical structure, hence it is perfectly intelligible, if the rate of carbon deposition is affected by the cause just mentioned, why the action should be much more energetic at one point than at another. Certain it is, that when pieces of calcined ore no larger than hemp seed are exposed under conditions favourable for becoming impregnated with carbon, the action is frequently so localized as to burst the ironstone into fine powder, the ore falling very much after the fashion of lime on being slaked. This bursting property, however, is by no means an invariable accompaniment of carbon impregnation, the morsels of ore frequently receivi a considerable charge of C without being in any way altered in form, the only apparent change being that of colour.

The Cleveland ore often consists essentially of three different kinds of stone.

A. Consisting of a porous mass interspersed with white specks.
B. Having a distinct slaty structure.
C. Do. do. but much harder.

A quantity of each in its raw state was placed in a combustion tube, A and C being at the ends and B in the middle, the whole being heated as equally as possible. CO was passed from A to C for 3½ hours and then reversed, and the current flowed from C to A for other 3½ hours.

		Fe in original stone.	Fe in stone after exposure.	Carbon per 100 Fe in in stone after exposure.
		Per cent.	Per cent.	Per cent.
Exp. 231.	A.	34·50	47·10	4·25
„ 232.	B.	30·30	40·40	5·44
„ 233.	C.	29·10	36·50	6·02

Thus, there appears a difference in the carbon depositing properties of these three varieties, but this difference does not appear due to the richness in iron, nor to the loss of weight during the operation, and would seem somewhat to confirm the opinion already expressed that texture rather than chemical composition is the cause.

I have formerly shown* that raw ironstone absorbed carbon much more readily than the same substance in its calcined state. Upon that occasion it was mentioned that while 100 parts of iron in the roasted ore, after 24 hours' immersion in the escaping gases of a blast furnace, took up 1·68 per cent. of C, 100 of Fe in the raw stone became impregnated with carbon to the extent of 4·63 per cent.

This fact has received ample confirmation since that time; two experiments may be instanced as an example of this.

Exp. 234. A sample of calcined Cleveland stone was exposed for 3½ hours to a current of perfectly dry and pure CO at a temperature just sufficient to soften zinc. At the end of the trial, 100 of metallic iron contained 2·14 of C.

Exp. 235. Unroasted ore was submitted to precisely the same treatment, after which, carbon, to the extent of 5·31 was associated with 100 of Fe.

It may be that the molecular state of the iron oxide in the two conditions of roasted and raw ore may alone account for this difference, or it may be, the change which carbonate of iron, as it exists in Cleveland stone, experiences on being heated may contribute, or indeed, be the sole cause of the superior power of the uncalcined stone to absorb C.

Exp. 236. Raw Cleveland stone, containing 88½ per cent. of its iron in the state of $Fe\,CO_3$, was heated to 200°C. (392°F.) in a current of N, when, apparently, the change was as follows:—

$$2\,Fe\,CO_3 = Fe\,O + CO + CO_2$$

as the resulting product contained almost the whole of its iron in the state of $Fe_2\,O_3$ (94 per cent.); so that the mere presence of nascent CO may form an important element in the amount of carbon deposited in the ore, but for this, fresh CO must be employed in addition, to neutralize the oxidising tendency of the large quantity of CO_2 present, as shewn by the equation.

Having thus briefly considered the manner in which mere differences of texture, as it were, appear to affect the infiltration of carbon into the pores of $Fe_2\,O_3$, or lower oxide, the manner in which the other cause of interference, viz., temperature, requires attention.

Carbon deposition has been shewn to commence at as low a tem-

* Transactions of Chemical Society, June, 1869.

perature as a little above 200° C. (392° F.) Now, so long as the carbon thus formed is not acted upon either by Fe_2O_3, or by the CO_2, generated by the action $2CO=C+CO_2$, it will go on accumulating in the oxide or ore in which it is being precipitated. It will now be proved that neither of these actions take place at the lower temperatures, and hence there is no cause at work to remove the C once formed.

A portion of a mixture consisting of—

C 52·14 per cent., Fe 35·13 per cent., and O 12·73 per cent.=100 obtained by passing CO over pure Fe_2O_3, and containing no metallic iron soluble in iodine and cold water, was thoroughly dried. This was placed in a porcelain tube, to which heat was applied, and, as the result of the action of C on an oxide of iron would be CO, and, probably, some CO_2, the gas generated by the action was conducted over heated CuO to convert it into CO_2, which was received in lime water to mark the first appearance of this substance. The lime water was contained in two bulbs, one (A) placed before the gas passed through the tube containing the heated cupric oxide, and the other behind it (B). Further, as the deoxidation of oxide of iron by carbon was known to be very slow at low temperatures, and the amount of CO generated, therefore, very small, a current of pure nitrogen was at command to sweep out the gaseous product of the action. The following are the results:—

Temperature.	A.	B.	Remarks.
Exp. 237. Zinc on top of tube not melted.	Cloudy in three minutes.	More cloudy than A in three min.	Action so slow that no evolution of gas on shuting off N.
Exp. 238. Zinc began to melt.	Cloudy in one minute.	Dense precipitate in one minute.	Still no evolution of gas when current of N suspended.
Exp. 239. Very low red heat.	Dense cloud in one minute.	Very dense precipitate in one minute.	Slow bubbles of gas when N was shut off.
Exp. 240. Low red heat	Slight precipitate in one minute.	Precipitate still more dense than in Exp.	Quick bubbles when N was shut off.

With a view to discover whether even a lower temperature than any of those just recorded might not suffice with longer exposure, to enable deposited carbon to act on oxide of iron, about one gramme of the mixture used in the previous experiments was placed in a hard glass tube of about three ccs. capacity, and all the air displaced by nitrogen. The tube was then sealed, and immersed in

an air bath, which was maintained at a temperature of 249° to 265° C. (480° to 510° F.)

Exp. 241. After an exposure of 4½ hours, the tube was removed and broken under mercury; 7 ccs. escaped, making 10 in all, and this, on analysis, was found to consist of—

CO_2	1·6
CO	70·4
N by difference ...	28·0
	100

Exp. 242. A second trial was made, similar to the first one, but with 8 hours' exposure. The issuing gas consisted of—

CO_2	7·1
CO	17·8
N by difference ...	75·1
	100

Exp. 243. At higher temperatures, the action of deposited carbon on any unreduced oxide of iron becomes much more rapid, CO chiefly being evolved. A portion of the same carbonaceous mass (C. 52·14, Fe 35·13, O 12·73) was heated in a stream of nitrogen for one hour, the temperature rising from coldness to red heat continued for a few minutes, and then falling again to coldness. Loss was 7·98 per cent. in weight: and, assuming only CO to be produced, this would represent 4·56 per cent. of oxygen driven off, or one-third of original oxygen was thus expelled as a minimum.

On treating the residual substance with iodine and cold water, an amount of iron was dissolved in two hours equal to 13·05 per cent. of the substance originally used, or, upwards of one-third of the whole iron present was reduced to the metallic state, and some compound of oxygen and iron, by the direct action of carbon.

This very powerful action of carbon, even at low temperatures, seems to render it probable that the formation of the small amount of metallic iron produced by the action of CO on Fe_2O_3, at the temperature of melting zinc, is really brought about by the carbon deposited, and not by the gaseous CO, and this view is corroborated by the fact, that in no instance has the formation of metallic iron by the action of CO on oxide of iron been observed without the simultaneous deposition of considerable quantities of carbon.

From what has preceded, it would not appear that there is any great difference between the temperature which suffices to produce

carbon deposition in an oxide of iron, and that where deoxidation commences. In experiment 200 the former action was shown to have been produced at very little above 200°C. (392°F.), whereas in experiment 13 deoxidation by CO commences at 141°C. (268°F.) It must be observed, however, that the means for detecting the latter operation, by cloudiness in lime water, was very delicate and instantaneous in its manifestation, while from the nature of the operation many hours, above twenty, were required to obtain a result sufficiently marked in its character. The maximum difference of temperature between the points where these two actions commence, may be stated to be 60°C. (108°F.); but I am by no means prepared to maintain that the phenomena of deoxidation and carbon deposition may not begin at the same temperature.

SECTION XII.—CIRCUMSTANCES WHICH LIMIT CARBON DEPOSITION.

The action which produces carbon in the operation under examination gives rise to the simultaneous generation of CO_2, and the temperature at which the gas commences to react on the deposited C must therefore impose a limit on the quantity obtained of the latter. To ascertain this, a quantity of calcined Cleveland ore which had been impregnated with C by exposure to the gas of a blast furnace for 144 hours, afforded aggregations of carbon, consisting chiefly of C and earthy matter. Of the former, the mass contained 64 per cent. of its weight.

Exp. 244. It was placed in a platinum boat, and all air expelled, by a continued current of pure and thoroughly dried CO_2, the unabsorbed portion being collected over mercury.

In 15 minutes the heat was fairly red, which speedily rose to bright red. After continuing the operation for 50 minutes 110 ccs. of unabsorbed gas was collected, which by explosion with oxygen and absorption by KHO, was found to consist of—

CO	76
N &c. from air probably in H Cl used in generating CO_2 ...	14
	—100

so that in all 83 ccs. of CO had been produced by the action of CO_2 on the deposited carbon.

Although the experiments just described prove that as the temperature rises, carbon which has been deposited may be carried

away, they afford no proof that at any temperature, however high, carbon impregnation does not take place. Indeed, at the highest heats applied to the oxide of iron (*vide* experiment 160), there was still a portion of C in the residual oxide and ore.

The facts disclosed by the last few experiments might suggest the inference, that under circumstances sufficiently favourable, CO might be entirely converted into C and CO_2. In the case of simple deoxidation, it has been shown (experiment 81) that CO can be entirely changed into CO_2, provided a very large excess of the oxidizing agent ($Fe_2 O_3$) is used, and that this complete conversion of the oxide of carbon into carbonic acid is only arrested by the oxide of iron losing so much of its oxygen as to establish a condition of equilibrium in relation to the composition of the atmosphere by which reduction is being effected.

What is now proposed to be considered is, whether the same law holds good in carbon deposition, *i.e.*, if an oxide of iron can decompose CO, no matter how much CO_2 may be present.

For the first experiments, Lancashire hæmatite and calcined Cleveland ore were selected as examples differing considerably in their power to withdraw C from CO (*vide* experiments 214 and 215). They were placed in separate tubes alongside of each other in a double Hoffman's gas furnace, by means of which they could be heated to a bright red. Previous to being so treated, both specimens had air aspirated over them while they were at a dull red heat.

The gas employed was that obtained from heating oxalic acid in sulphuric acid, and consisting, therefore, of equal volumes of CO and CO_2. All air being expelled, heat was applied, and continued at the maximum power of the furnace for one hour.

	Substance used.	Carbon deposited.	Percentage of Original O Lost.
Exp. 245.	Lancashire ore	Nil	30·9
„ 246.	Calcd. Clev. do.	„	33·7

The effect of a longer exposure was next tried, viz., 5½ hours instead of one hour, the temperature being maintained the same as in experiments 245 and 246:—

	Substance used.	Carbon deposited.	Percentage of Original O Lost.
Exp. 247.	Lancashire ore	Nil	41·8
„ 248	Calcd. Clev. do.	Nil	50·8

The same experiments were repeated—zinc melting on top of tubes, but they themselves not visibly red hot—temperature possibly about 450°C. (832°F). In this case the operation was continued for three hours.

	Substance used.	Carbon deposited.	Percentage of Original O Lost.
Exp. 249.	Lancashire ore	Nil.	34·8
„ 250.	Calcd. Clev.	„	35·6

At a temperature of 260° to 288°C. (500° to 550°F.) by exposure in the air bath for six hours, the following figures were obtained:—

	Substance used.	Carbon deposited.	Percentage of Original O Lost.
Exp. 251.	Lancashire ore	Nil.	18·5
„ 252.	Calcd. Clev.	„	8·8

The power of precipitated anhydrous Fe_2O_3 to split up CO in a mixture of equal volumes of this gas and CO_2 was then experimented upon at a heat, fairly red.

	Grammes.		
Exp. 253.	1·348 of the oxide after 2 hrs.	weighed	1·222 grs.
	„ after 2 hrs. more	„	1·220 „
	„ „	„	1·219 „

No carbon was obtained in the residue. The amount of oxygen removed was 32·2 per cent. of that originally in the Fe_2O_3. Having regard to the fact that this loss was not increased during the last 2 hours, and very imperceptibly so during the last 4 hours, equal volumes of CO and CO_2 may be considered as inert in affording C by the decomposition of CO in this, or any other of the temperatures just enumerated.

The proportion of CO_2 was now reduced to 50 vol. per 100 of CO—actually the gas used on analysis was found to consist of—

CO	66·7 volumes.
CO_2	33·0 „
Air, &c.	0·3 „
	——100

The lead bath arrangement was employed, and the following substances were simultaneously exposed to the above mixture, at a

temperature sufficient to soften zinc, about 410°C. (770°F.) for 5½ hours.

	Substance used.	Carbon precipitated per 100 of Fe.	Per cent. of original oxygen removed.
Exp. 254.	Clev. calcd. ore	Nil. ...	... 2·2
„ 255.	Fe_2O_3 from calcd. Fe SO_4	„ ...	... 7·9
„ 256.	Fe_2O_3 precipitated anhydrous	„ ...	... 6·7
„ 257.	Fe_2O_3 from nitrate	„ ...	... 5·6

The above were returned to the lead bath on the following day, and the operation was continued for five hours more, making in all 10½ hours; the temperature being the same, viz., about 410°C. (778°F.)

	Substance used.	Carbon precipitated per 100 of Fe.	Per cent. of original oxygen lost.
Exp. 258.	Clev. calcd. ore	Nil. ...	... 10·0
„ 259.	Fe_2O_3 from calcd. Fe SO_4	trace ...	... 11·2
„ 260.	Do. precipitated anhydrous	0·9 ...	... 32·7
„ 261.	Do. from nitrate ...	6·4 ...	... 37·8

The effect of the second exposure being so much more marked than the first, at all events, in the case of pure Fe_2O_3, it seems probable the heat in the former one has not been so well maintained, or the results may have been modified by the rate of the current as explained in experiments 146 to 157.

In tubes placed side by side in the double Hoffman's furnace at a very dull red heat, the same mixture of gas (100 CO 50 CO_2), gave in six hours:—

	Substance used.	Carbon per 100 Fe.	Per cent. of original oxygen lost.
Exp. 262.	Clev. calcd. ore	1·5 ...	... 13·5
„ 263.	Precipitated anhydrous Fe_2O_3	1·5 ...	... 45·8

These two sets of experiments, viz., with CO_2 and CO in equal volumes, and with CO_2 in the proportion of one volume to two of CO would show that whereas at any temperature the former, viz., equal volumes of each, no carbon deposition is possible, that with the latter we are just on the verge of those proportions where the appearance of C begins.

Measures were now taken to obtain, as nearly as might be, a mixture of CO_2 to three of CO, so as to ascertain its increased power

of conferring carbon upon oxide of iron. The composition of the associated gases was found to be—

CO	76·0 volumes.
CO_2	23·6 „
Air, &c., by difference	·4 „
	——100

	Substance used.	Carbon per 100 Fe.	Per cent. of original oxygen lost.
Exp. 264.	Calcd. Clev. ore	Nil.	... ... 4·4
„ 265.	Raw „	trace.	... not ascertained.
„ 266.	Precipitated Fe_2O_3 anhydrous	9·3	... 62·1

The above were exposed for five hours in the lead bath, during which time the maximum temperature was that indicated by zinc, softening probably 410°C. (770°F.)

On the following day the same samples were subjected to an additional exposure of 5½ hours, making in all 10½ hours, the maximum temperature being like that in the former case 410°C. (770°F.)

	Substance used.	Carbon per 100 Fe.	Per cent. of original oxygen lost.
Exp. 267.	Calcd. Clev. ore	Nil.	... ... 6·8
„ 268.	Raw „	trace.	... not ascertained.
„ 269.	Precipitated Fe_2O_3 anhydrous	9·0	... ... 18·7

In this case the second exposure has practically added no carbon, and possibly from the temperature being somewhat higher than in experiments 264 to 266, a considerable amount of reoxidation has taken place.

In describing the action of CO upon oxides of iron, the increased activity of the gas has been remarked on, when it was passed in a more rapid stream over the iron oxide exposed to its action.

Exp. 270. The same mixture of gases, when passed over calcined Cleveland ore, at a dull red heat, for 5 hours, afforded 1·5 of carbon per 100 of Fe present, and removed 70 per cent. of the original oxygen; under the same circumstances, precipitated Fe_2O_3 deposited 0·9 of carbon per 100 of Fe present, while 90 per cent. of the original oxygen was removed.

This has been observed, both in respect to reduction and to carbon impregnation. The extent to which the presence of CO_2 in the reducing gas modifies the action, has just been explained, and in the belief that the change in amount of reduction, &c., was due to

the difference of effect produced on the composition of the current of gas itself, steps were taken to ascertain the precise nature of the alteration experienced by the CO. It might have been inferred from what has just been stated, that although a larger amount of oxygen had been withdrawn from the ore in the case of the rapid current of gas, and, consequently, a larger amount of CO_2 generated, yet, in consequence of the larger volume of CO employed in the trials, the relation between these two gases was more favourable for reduction and carbon deposition, in consequence of the larger percentage of the last named gas.

The following are the data upon which the calculations are based:—Six samples of ironstone, differing considerably in their physical condition, were bruised to powder, and two grammes of each were placed in the lead bath arrangement. Twelve grammes were thus simultaneously exposed for 6 hours, in which zinc softened 410°C. (770°F.) Over this, 65 litres of CO were passed, with the precautions observed on previous occasions.

After this, 12 grammes of the same specimens placed in the same relative position in the lead bath, had 213 litres of CO passed over them in the same period of time, and the temperature being maintained the same as before, viz., that of softening zinc.

The specimens are named after the first six letters of the alphabet:—

Substance employed.	Slow current.			Rapid current.		
		Per cent. of O removed.	C. per 100 Fe.		Per cent. of O removed.	C. per 100 Fe.
Ironstone calcined *a* ...	Exp. 271	14·0 ...	20·	Exp. 277	26·6 ...	71·5
Do. do. *b* ...	,, 272	31·7 ...	44·3	,, 278	43·2 ...	125·6
Do. do. *c* ...	,, 273	30·4 ...	40·7	,, 279	35·5 ...	195·3
Do. do. *d* ...	,, 274	18· ...	26·4	,, 280	58·8 ...	358·5
Do. do. *e* ...	,, 275	18·4 ...	16·4	,, 281	58·6 ...	140·6
Do. do. *f* ...	,, 276	7·4 ...	7	,, 282	30·3 ...	82·4

The average of the six trials:—

	Slow current.	Rapid current.
Percentage of Oxygen removed	19·9	42·1
Carbon per 100 Fe deposited	24·7	179·0

The following statement exhibits the nature of the change

experienced by the two portions of gas passed over these six samples of iron ore in six hours:—

	Slow current.	Rapid current.
Litres of gas employed measured at 0°C. and 760 m.m. pressure...	65	213
Weight of gas in grammes	81	266
	Grammes.	Grammes.
Containing of carbon	34·7	114·0
If all the CO were converted to CO_2, it would take up of oxygen	46·3	152·0
And would furnish of CO_2	127·3	418·0
Oxygen actually taken up was	0·41	0·86
Carbon actually deposited was	1·19	8·59
		grms
Weight of CO_2 formed by reduction	$(\frac{11}{4} \times 0{\cdot}41$ grms$) = 1{\cdot}13$	$(\frac{11}{4} \times 0{\cdot}86$ grms$) = 2{\cdot}36$
Do. formed by reaction of $2\,CO = C + CO_2$	$(\frac{11}{3} \times 1{\cdot}19$ grms$) = 4{\cdot}36$	$(\frac{11}{3} \times 8{\cdot}59$ grms$) = 31{\cdot}49$
Total CO_2 formed ...	5·49 grms.	33·85
This corresponds to CO	3·49 „	21·54
Hence the unaltered CO was	77·51 „	244·46
	81·00 „	266·00
Hence the average composition of the gases after they had done their work, for 100 parts by weight of CO, would be of CO_2	$(\frac{100}{77{\cdot}51} \times 5{\cdot}49) = 7{\cdot}09$	$(\frac{100}{244{\cdot}46} \times 33{\cdot}85) = 13{\cdot}84$
Ratio of oxygen removed to total which CO could absorb if all were changed into CO_2	$\frac{0{\cdot}41}{46{\cdot}3} = 0{\cdot}89$ per cent.	per cent. $\frac{0{\cdot}86}{152} = 0{\cdot}56$

Ratio of Carbon deposited to that contained in the CO used	$\frac{1{\cdot}19}{34{\cdot}7} = 3{\cdot}43$ per cent.	$\frac{8{\cdot}89}{114{\cdot}0} = 7{\cdot}54$
Ratio of CO_2 produced to that which the whole CO could produce	$\frac{5{\cdot}49}{127{\cdot}3} = 4{\cdot}32$ „	$\frac{33{\cdot}86}{418{\cdot}0} = 8{\cdot}10$

We, therefore, have had in these experiments a mixture of gases removing above twice as much oxygen, and depositing seven and a quarter times as much carbon, in the same space of time, as another mixture of a far more energetic composition in respect to reducing and carbon impregnating powers.

Two modes of explanation occur to me to account for this apparent anomaly.

In experiment 17, calcined Cleveland ironstone suffered marked reduction at 210°C. (401°F.), whereas (experiment 71) metallic iron had no effect on CO_2 at 299°C. (570°F.)

Perhaps the following trial may exhibit, in an intelligible form, the relative powers of CO, to deprive iron ore of its oxygen, and of metallic iron to decompose the resulting carbonic acid.

Exp. 283. About ten grammes of ores of different kinds were placed in the lead bath apparatus, and pure CO passed over them for six hours. The total quantity of gas used was 170 litres, and on ascertaining the total quantity of oxygen displaced, the composition of the issuing gas would be about 92 parts by weight of CO to 8 of CO_2.

Among the ores was a specimen of Lancashire hæmatite containing nearly 67 per cent. of Fe, therefore nearly pure Fe_2O_3, and along with it, was one specimen of the same ore, perfectly reduced in hydrogen, as well as a sample of pure spongy iron.

During the experiment zinc had melted, but antimony remained unchanged. At its conclusion, the hæmatite was found to have lost 73 per cent. of its original oxygen, while the reduced hæmatite had only absorbed 17 per cent., and the spongy iron 11 per cent. of the oxygen required to convert them into Fe_2O_3. Let us assume 200°C. (392°F.) to be the temperature of no action by CO on Fe_2O_3, and 300°C. (572°F.), that when CO_2 is not affected by Fe. Between these points and the degree of heat required to fuse zinc, 417°C. (782°F.), the reducing power of CO may be expressed by

73, and the oxidizing power of CO_2 on metallic iron by 17, or as 4·3 to 1 in an atmosphere of 92 of CO to 8 of CO_2 by weight.

Under the circumstances described, the reduction of Fe_2O_3 and the oxidation of Fe were effected at the same temperature, say melting zinc, it is therefore clear that to rob the one of as much oxygen as is conferred on the other, the reducing atmosphere could afford to be charged with a larger proportion of CO_2 than the oxidizing one.

Now, in the case under consideration, the addition of 217°C. (*i.e.* 200 to 417C°.) has produced the change, and it is therefore obvious that even 10°C. may, at a particular period, greatly affect the power of CO to reduce iron, and enable it, at certain temperatures, to do so more readily even in presence of a larger quantity of CO_2, than it was associated with previous to the supposed addition of ten to thirty degrees of heat.

It is probable that the deoxidation of iron oxide is accompanied by a slight rise in temperature, that is to say, the heat developed by the conversion of CO into CO_2, is greater than the absorption of heat by the gasification of the O contained in the oxide of iron.

From the nature of things, the temperature of iron oxide suffering rapid reduction will rise more than if the same operation were conducted more slowly, just as the slow rusting of iron is accompanied by no appreciable elevation of temperature, while the rapid oxidation of the same metal gives intense heat in a Bessemer converter.

To a small rise in temperature, not amounting to the difference between that required to melt zinc and fuse antimony may possibly be ascribed an increase in the energy of a current of CO passed rapidly over Fe_2O_3, although it is accompanied by a larger proportion of CO_2.

The other explanation of the anomaly is the following:—

The CO_2 produced, being heavier than the CO, would have a tendency to accumulate at the bottom of the vessel; hence, the CO_2 in the immediate vicinity of the specimens exposed, probably, considerably exceeded the average amount contained in the whole gas. In the experiment with the more rapid current, this accumulation would, possibly, be more rapidly swept away—from the greater circulation of gaseous currents within the vessel, so that it is quite possible that the gas surrounding the specimens in the case of the

slow current was really richer in Co_2 than that of the rapid current.

Whichever of these two explanations be accepted, it is obvious that moderate changes in temperature, or in the composition of the gases, or of both, effect a material alteration in the character of the result.

I have been at some pains to direct particular attention to the effect produced by a not very great elevation of temperature upon the reducing and carbon depositing powers of CO, and upon the oxidizing power of CO_2. Up to a certain point the former increases the more rapidly; but there are, as we have seen, other temperatures (experiments 79 and 80), in which a precisely opposite effect is produced, and at which the power of CO is overcome by that of CO_2; and as both these changes will be hereafter shown to have a distinct practical value in the blast furnace, it is desirable both should be well kept in view.

The fact, that no experiment has been successful in obtaining substances free from O by the action of CO on Fe_2O_3 at temperatures close upon that of melting zinc, seems to indicate that at this temperature, the oxidizing action of CO and CO_2 jointly is apparently equal to the reducing action of C and CO on the mixture of Fe and unknown oxides, F_xO_y produced by the previous reduction of Fe_2O_3; while, on the other hand, the large increase in deposited carbon visible on re-exposing a sample of reduced and carbon-impregnated iron oxide to the action of CO (experiment 206 and 207), appears to indicate that at this temperature the tendencies towards C deposition are more powerful than towards C gasification.

At a bright red heat, a different state of things prevails—pure precipitated Fe_2O_3 was wholly reduced by H, and exposed to the action of CO at a bright red, and the original Fe^3O_3 was similarly exposed, with the following results:—

		Exp. 284. Pure Fe_2O_3	Exp. 285. Spongy iron.	Exp. 286.
Time of exposure:		Five hours.	One hour.	Four hours.
Composition...	Fe	99·33	99·20	99·34
	O	·43	·48	·30
	C	·24	·32	·36
		100·	100·	100·

We may therefore infer that a position of equilibrium has been nearly arrived at, the composition of the inert substance being almost identical in all the three cases.

The small quantity of C in the mixture shows how energetic is the action of C in the oxide $Fe_x O_y$,—the carbon deposited being again gasified almost as quickly as it is produced.

Similar results, as regards carbon impregnation, were obtained with Cleveland calcined ironstone.

The following numbers show how the carbon gasifying tendencies increase relatively as the temperature rises using this ore:

	Temperature.	Hours of exposure.	C per 100 Fe present.
Exp. 287.	Just below red	...4½	57·6
	Low red to bright red	...21 see exp. 228.	2·3
„ 288.	Bright red	... 1	1·3
	Very bright red	... 4½ see exp. 229.	·3
„ 289.	White heat	... ⅝	0·3

It therefore appears highly probable that certain conflicting tendencies may balance one another, and ultimately yield a substance upon which CO is absolutely inert. The composition attained, when such is the case, will manifestly depend on the temperature, and probably, on the molecular condition of the $Fe_2 O_3$ employed in the first instance.

The experiments, 271 to 282, afford a convenient opportunity of pointing out that the extent of carbon deposition bears no necessary relation to the amount of oxygen removed. To illustrate this, there is placed in the subjoined columns, the extent of carbon deposition, and the percentage of original oxygen the ore has lost. The specimens, for convenience sake, are ranged in the order of carbon deposition, beginning with the highest:—

Slow current of CO.	Carbon per 100 Fe.	Original O removed.
Ore marked *b*	... 44·3	... 31·7 per cent.
do. *c*	... 40·7	... 30·4 „
do. *d*	... 26·4	... 18·0 „
do. *a*	... 20·0	... 14·0 „
do. *e*	... 16·4	... 18·4 „
do. *f*	... 0·7	... 7·4 „
Rapid Current of CO.		
Ore marked *d*	... 358·5	... 58·8 „
do. *c*	... 195·3	... 35·5 „
do. *e*	... 140·6	... 58·6 „
do. *b*	... 125·6	... 43·2 „
do. *f*	... 82·4	... 30·3 „
do. *a*	... 71·5	... 26·6 „

All these specimens were of one description of ore, differently calcined, for reasons which will be hereafter explained, but the same law as that now mentioned, will be seen to hold good with other iron compounds.

	Slow current of CO.	Per cent.	Carbon per 100 Fe	Original oxygen removed. Per cent.
Exp. 290.	Fe_2O_3 from calcd. $FeSO_4$	70 Fe ...	90·9	... 60·9
„ 291.	do. precipitated ...	70 ...	78·7	... 49·3
„ 292.	Lancashire hæmatite	66·6 ...	60·1	... 36·0
„ 293.	Clev. calcd.	40·0 ...	12·6	... 37·3
„ 294.	Elba ore	66·8 ...	3·8	... 16·9
„ 295.	Spathose calcined ...	51·7 ...	2·3	... 13·0
	Rapid current of CO.			
Exp. 296.	Fe_2O_3 from $FeSO_4$ ...	... ...	476·5	... 72·6
„ 297.	do. precipitated ...	... ...	335·4	... 80·6
„ 298.	Lancashire hæmatite	... ...	270·8	... 71·0
„ 299.	Clev. calcd. ...	... ...	22·3	... 50·7
„ 300.	Elba ore ...	... ...	4·9	... 18·2
„ 301.	Spathose roasted ...	... ...	3·9	... 42·0

These two series of trials were made on the same ores, and were both exposed, in respect to time and temperature under the same conditions, viz., zinc softened, and antimony unaltered. In the case of the slow current, 63 litres were consumed, and in the other, 248 litres. In these, as in experiments 271 to 282, every specimen in each trial occupied the same position in the lead bath, so that, as far as possible, the same relative temperatures might be secured.

The average of the six trials gave :—

	Slow current.	Rapid current.
Percentage of oxygen removed	35·5 ...	55·8
Carbon per 100 Fe deposited	41·4 ...	185·6

Underneath is appended a tabular statement of the nature of the change in the two currents of gas, resembling that given when describing experiments 271 and 282.

	Slow current.	Rapid current.
Litres of gas employed measured at 0°C and 760 m.m. pressure...	63	248
Weight of Gas in grammes	79	310

	Grammes.	Grammes.
Containing of Carbon	33·9	132·9
If all this CO were converted into CO_2 it would take up of Oxygen	45·1	177·1
And would furnish of CO_2	124·1	487·1
Oxygen actually taken up	1·124	1·745
Carbon actually deposited	3·02	13·45
Weight of CO_2 formed by reduction	$(\frac{11}{4} \times 1{\cdot}124) = 3{\cdot}09$	$(\frac{11}{4} \times 1{\cdot}745) = 4{\cdot}80$
Weight of CO_2 formed by re-action 2 CO = C + CO_2	$(\frac{11}{3} \times 3{\cdot}02) = 11{\cdot}07$	$(\frac{11}{3} \times 13{\cdot}45) = 49{\cdot}32$
Total CO_2 formed	14·16	54·12
Corresponding to CO	9·01	34·44
Hence the unaltered CO was	69·79	275·56
Hence the average composition of the gases after they had done their work, for 100 parts by weight of CO would be of CO_2	$(\frac{100}{69{\cdot}79} \times 14{\cdot}16) = 20{\cdot}23$	$(\frac{100}{275{\cdot}56} \times 54{\cdot}12) = 19{\cdot}64$
Ratio of oxygen removed to total which CO could absorb if it were all changed into CO_2	$\frac{1{\cdot}124}{45{\cdot}1} = 2{\cdot}50$ per cent.	$\frac{1{\cdot}745}{177{\cdot}1} = 0{\cdot}99$ per cent.
Ratio of Carbon deposited to that contained in the CO used	$\frac{3{\cdot}02}{33{\cdot}9} = 8{\cdot}91$ „	$\frac{13{\cdot}45}{132{\cdot}9} = 10{\cdot}12$ „
Ratio of CO_2 formed to that which the whole CO could produce	$\frac{14{\cdot}16}{124{\cdot}1} = 11{\cdot}41$ „	$\frac{54{\cdot}12}{487{\cdot}1} = 11{\cdot}11$ „

Here, it will be seen, the issuing gases had, as nearly as may be, the same composition in both cases, but then it must not be overlooked,

that in the instance of the slow current, these particular ores were nearly as energetic, in respect to reduction, as those used in experiments 271 to 282 were, with the rapid stream of CO, the figures being—

Percentage of O removed.	Slow current.	Rapid current.
In experiments 271 to 282, ...	19·9 ...	42·1
„ 290 „ 301, ...	35·5 ...	55·8

Comparatively, the carbon deposited for 100 Fe present was as follows:—

In experiments 271 to 282, ...	24·7 ...	179·1
„ 290 „ 301, ...	41·4 ...	185·6

It would, therefore, seem reasonable to infer that the precise temperature for maximum effect was not the same in the six specimens of Cleveland stone, *a. b. c. d. e. f.*, and the six compounds of peroxide of iron given in the last quoted experiments.

In the experiments last described, the issuing gases in the case of the slow and rapid currents were both practically the same in point of composition, for those of the former contained 20·23 per cent., and those of the latter 19·64 per cent. of CO_2, so that neither of these disturbing causes attending experiments 271 to 282 appears to have obtained here.

It is, however, worthy of remark, that a specimen of calcined Cleveland ore, from the same sample, behaved very differently in the two series of experiments, thus:—

					Lost of original O.	C deposited per 100 Fe.
In Exp. 271, with slow current, in an atmosphere containing			7·09	per ct. CO_2	14·0	20·0
„ 293, do.	do.	do.	20·23	„ „	37·3	12·6
„ 277, do.	rapid current		13·84	„ „	26·6	71·5
„ 299, do.	do.		19·64	„ „	50·7	22·3

It would, therefore, seem probable that some slight difference of temperature, from whatever cause proceeding, must have been at work here, inasmuch as the rapid current was considered as affecting the result by producing a quicker circulation of the gases, and a more rapid removal of the CO_2, generated by the action. But this latter circumstance could scarcely affect experiments 293 (slow current), and 299 (rapid current), for in the former, with 20·23 per cent. of CO_2 in the issuing gases, 37·3 per cent. of O was removed, and 12·6 of C deposited, and in the latter, the CO_2 existed to the

extent of 19·64 per cent. in the issuing gases, while the O removed amounted to 50·7 per cent., and carbon deposition to 22·3.

SECTION XIII.—CARBON DEPOSITION AS EFFECTED BY BLAST FURNACE GASES.

The imprudence of permitting the gases of a blast furnace to leave the throat, so long as they are able to communicate heat to the incoming materials or deoxidize the ore, has been already adverted to.

If this source of loss as regards reduction of iron oxide is guarded against, no waste of fuel can result from any unexhausted power of carbon deposition. It is easy to show that the mere act of dissociation of CO into C and CO_2 is a heat-producing change, for we have

1 of C as CO burnt to CO_2—affording	5,600	units.
Less 1 of C as CO reduced to C—absorbing	2,400	„
Leaving a balance of	3,200	„

Any loss of heat, however, from not securing carbon deposition over as long a period as possible, cannot take place, if the gases leave the furnace in a condition no longer fit for deoxidizing the ore, for the simple reason that a temperature insufficient for reduction is unable to separate carbon from CO, and the presence of CO_2 in the mixed gases puts an end to carbon deposition sooner than it does to removing oxygen from iron oxide.

It will, nevertheless, be interesting to pursue the same train of inquiry as to the power possessed by the furnace gases in impregnating iron ore with carbon, as was done in the matter of reduction.

A quantity of Cleveland ironstone, containing 40 per cent. of Fe was broken into pieces, the size of hazel nuts, and several fragments of these were exposed for an hour in the gas exit pipes of four different furnaces at the Clarence Works. The usual *average* composition of the gases emitted by these furnaces is given, but it by no means follows that this corresponds exactly with that at the time of these particular experiments. So far as practicable, the external crust of each piece of ironstone, at the end of the trials, was removed to prevent any adhering impurity contracted during the exposure interfering with the results.

	Furnace.	Vols. CO_2 per 100 CO.	Temperature. Lead.	Zinc.	Per cent. Fe after exposure.	C per 100 Fe present.
Exp. 302.	6,000 c. ft.	19	Melted	Melted	40·4	1·28
,, 303.	11,600 ,,	42	Softened		40·3	·96
,, 304.	15,500 ,,	42	,,		40·4	·92
,, 305.	25,500 ,,	42	,,		40·3	1·00

Similar trials were made in which the exposure of calcined Cleveland ore was continued over several hours.

	Furnace.	Vol. CO_2 per 100 vol. CO.	Hours Exposed.	Temperature. Lead.	Zinc.	Antmy.	Fe before Exposure. per cent.	Fe after Expos.	C per 100 Fe.
Exp. 306	6,000 c. ft.	19	24	Melted	Soft	...	40·8	43·2	1·96
,, 307	,,	,,	24	,,	Melted	Soft	39·13	41·6	2·40
,, 308	,,	,,	48	,,	,,	,,		42·5	2·42
,, 309	,,	,,	72	,,	,,	Melted		42·77	3·11
,, 310	,,	,,	96	,,	,,	,,		43·10	2·64
,, 311	25,500 c. ft.	42	24	,,	Nil.		38·84	39·13	trace.
,, 312	,,	,,	48	,,	,,			39·28	,,
,, 313	,,	,,	72	,,	,,			41·00	,,
,, 314	,,	,,	96	Bismuth melted, lead not				40·96	,,

In experiments 306 to 310, the residuum left after treatment with hydrochloric acid was deep black, whereas, in the four succeeding trials, the residue was a light grey, and contained a mere trace of carbon.

To compare the power of raw and calcined ironstone to deposit carbon, a trial was made in the escaping gases from the furnace of 6,000 cubic feet, having a probable composition and temperature as given above.

		100 of calcd. ironstone contained of carbon.	100 of raw ironstone contained of carbon.
Exp. 315.	After 24 hours' expos. ...	·4	1·5
,, 316.	,, 168 ,, ...	1·0	7·8

The method pursued to determine the carbon in these trials consisted in dissolving out the iron, &c., by means of hydrochloric acid. The insoluble portion containing the carbon was collected on a filter of asbestos and dried. This was placed in a combustion tube, and heated in a stream of oxygen, and the gases produced were conducted through a second tube containing red hot oxide of copper, to ensure the complete conversion of CO into CO_2. The carbonic acid properly dried by $Ca\,Cl_2$, was absorbed in a potash bulb, weighed, and the weight of C calculated therefrom.

A specimen of Rhenish spathose ore, previously calcined, was then compared with roasted Cleveland ironstone, also, in the gases of a furnace of 6,000 cubic feet.

Exp. 317. The following was the composition of the latter, previous to exposure for 24 hours, during which time zinc had melted.

Fe	44·77
O	19·19
Earths	36·04
	—— 100

After exposure, it contained :—

Fe	46·40
O	17·40
C	1·08
Earths	35·12
	—— 100

In which 100 of Fe present was associated with 2·33 of carbon.

The spathose ore, on being removed, being in coarse and fine powder, could not be properly separated from the dust which is found in large quantities in the escaping gases. To avoid contamination from this source, the fine dust was separated from the larger particles, and the two were tested for carbon :—

100 of the fine dust contained 8·09 of carbon.
„ coarse pieces „ 16·85 do.

This ore, previous to exposure, consisted of—

Fe	58·00
O	24·85
Earths	17·15
	—— 100

Subsequent to exposure, its composition was—

Fe	51·00
O	17·07
C	16·85
Earths	15·08
	—— 100

And in which the carbon amounts to 33·04 per cent. of the Fe present. The exposure lasted for 24 hours, during which time antimony had fused.

The power of carbon impregnation possessed by gases taken from different depths of a furnace of 6,000 cubic feet, was next made the subject of inquiry. Specimens of calcined Cleveland ironstone were placed in a tube, as was practised when trying the reducing power of the gases, and exposed during a period of two hours. On being withdrawn, they were immediately transferred to a bottle, and sealed up.

	Distance from top.		Temperature.	Carbon deposited per 100 Fe present.
Exp. 318.	4ft.	3 in.	No signs of redness ...	3·07
„ 319.	9	9	Cherry red	0·56
„ 320.	15	9	Bright red	0·32
„ 321.	21	5	Very bright red	0·55
„ 322.	27	3	do.	0·32

The numbers afforded by these five experiments are confirmatory of the law already laid down, in respect to the rapid decrease of carbon deposition at higher temperatures, and this, notwithstanding the greater richness in CO at points where the heat is the most intense.

The usual composition of gases taken from these levels, and the removal of oxygen in the particular cases just given, were as follows :—

	From top.		Usual Composition of Gas.		Percentage of original oxygen removed.
Exp. 323.	4ft.	3in.	21 vols. Co_2 per 100 vols.	CO ...	13·7
„ 324.	9	9	5 do.	do. ...	76·2
„ 325.	15	9	0 do.	do. ...	76·3
„ 326.	21	5	6 do.	do. ...	68.2
„ 327.	27	3	9 do.	do. ...	68·1

In seeking to ascertain the power of reduced spongy iron to split up CO, when the gas was tolerably pure, there was a difficulty in preserving the iron from oxidation when it was withdrawn from the furnace, but, from the precautions taken, this, probably, would not materially affect the amount of carbon the metal had absorbed.

Exp. 328. A specimen of the spongy iron was exposed at a point in a furnace of 17,500 cubic feet, 55 feet from the top, for 1½ hours. The temperature was bright red.

Exp. 329.—The composition of gas at the point where the trial

was made, according to analyses made before and after the experiment:—

CO_2	...	...	2·7	...	4·9
CO	...	...	31·5	...	28·5
H	...	...	Nil.	...	1·4
N	...	...	65·8	...	65·2
			100		100

The iron was a specimen of Fe_2O_3, obtained by calcination of $FeSO_4$, reduced until 100 of Fe was associated with 3·6 of O.

The closed end of the tube, in which it was exposed, was perforated for 6 inches of its length with holes 0·1 inch in diameter, and this portion was filled with pumice-stone, to intercept fume, which, by coating the iron, might possibly interfere with carbon deposition and estimation. Two ounces of metal occupied a space 12 inches long in the tube, separated from the pumice by an iron plug, fitting loosely, so as to permit gases to pass through.

The portion of the pipe, in which the iron lay, did not reach into the furnace, but the temperature was such that it was a pretty bright red in the sunshine.

At the termination of the exposure, which lasted 4½ hours, next the furnace, 100 of Fe, was found associated with ·99 of C and the iron, probably from the CO_2 in the gas, and from another cause which will receive immediate attention, had increased the oxygen from 3·6 to 4·5 per 100 of Fe. The iron at the extremity next the air, which was excluded as much as possible, contained 9·53 of O per 100 of Fe, and, possibly from the heat being lower there, had absorbed 1·50 of carbon.

Exp. 330. A few days after these trials, the experiment was repeated with the same sample of spongy iron. It was exposed for 4½ hours to the gases as they leave the furnace, and containing, therefore, a considerable quantity of CO_2, which would tend to oxidise the iron. The temperature would vary from the melting point of zinc to that of lead.

In this case it was the portion of the ore nearest the furnace that was most highly oxidized. It had 100 of Fe united with 9·2 of oxygen, whereas that at the other end contained only 6·2 of oxygen. The amounts of carbon were 0·2, and ·35 for 100 of Fe respectively.

These experiments upon metallic iron and Fe_2O_3, when exposed to contact with heated furnace gases, indicate that the metal in

the form of oxide acts more energetically than it does when in the reduced form—a state of things which corresponds, as will be seen immediately, with the trials made with pure CO and mixtures of CO and CO_2 in the laboratory. It would therefore appear erroneous to maintain, as has been done, that reduced metal is necessary for carbon impregnation. On the contrary, experiments will be quoted to prove that carbonic oxide can be split up into CO_2 and C without any metallic iron being present.

SECTION XIV.—CHANGE EXPERIENCED BY METALLIC IRON AND BY IRON OXIDES WHICH HAVE SERVED TO DISSOCIATE CO.

Having thus explained at some length the nature of the influence of temperature, and of carbonic acid on carbon impregnation by CO of Fe_2O_3, either factitious or native, we may now proceed to consider the behaviour of the iron oxide which, assisted by heat, has brought about the splitting up of the carbonic oxide.

A priori, this deposition of carbon might appear to be caused by the action of spongy metallic iron, formed by the action of CO in ferric oxide on another portion of CO, thus re-forming some iron oxide of unknown composition—$Fe_x O_y$, and this reformed oxide, being probably again reduced as fast as formed, so that the reactions are:—

$$x\ Fe + y\ CO = y\ C + Fe_x O_y, \text{ and then}$$
$$Fe_x O_y + y\ CO = y\ CO_2 + Fe_x$$

which are, on the whole, equivalent to $2\ CO = C + CO_2$, the equation formerly given as representing the final action.*

Viewing the existence of metallic iron as possibly an essential condition for producing carbon impregnation, means were taken to ascertain the conduct of this substance in the spongy, as well as in its denser condition, when exposed to heated carbonic oxide.

Exp. 331. A weighed quantity of pure Fe_2O_3 was placed in a boat in a porcelain tube, heated by a Hoffman's furnace. By means of a T tube, furnished with screw pinch-cocks, either H or

* This action may account for the formation of steel from malleable iron, the occluding power of iron for CO at acieration temperatures, being probably an important property in this respect.

CO could be admitted at pleasure from their respective sources, viz., zinc and sulphuric acid for the one, and ferro cyanide of potassium and sulphuric acid for the other. The precautions formerly spoken of were employed for purifying and drying the gases, and which, therefore, may be assumed as arriving at the Fe_2O_3 in a perfectly pure state. All air was expelled from the apparatus, CO generator included, by a long continued stream of hydrogen; the porcelain tube was then heated, and the H_2O produced collected and weighed. During this time the CO generator was giving off CO, but the gas was permitted to escape through a side valve. When the ferric oxide was completely reduced (known by no more H_2O being produced after several minutes' passage of H), the H was shut off, and the CO turned on.

5·487 grammes of pure Fe_2O_3, exposed to H, gave H_2O 1·858 grms.
the theoretical quantity of H_2O being ... ... 1·852 „

CO was then passed over the reduced iron, for 4½ hours, at a temperature of melting zinc—the residual mass was dissolved in HCl, and the carbon left weighed ·78 grm., equal to 20·3 per cent. of the Fe present.

Exp. 332. 3·497 grammes of pure Fe_2O_3, heated in H, yielded

in one hour of	...	...	...	H_2O, 1·189
„ ten minutes more, additional			...	... ·001
„ do.	do. ...	...	...	nil.
		Total	...	1·190

Theoretical water being 1·1802

CO passed over it, for one hour, at a very dull red heat, gave of carbon, ·0584, equal to 23·8 per cent. on the Fe.

Exp. 333. 3·497 grammes of pure Fe_2O_3 gave same results as above, when treated with H, no more H_2O being produced after 25 minutes' passage of gas, The spongy iron was then exposed to CO at a low, red heat for 2½. hours. The carbon deposited was determined by combustion in oxygen, with a tube in front, containing red hot Cu O, to prevent loss by formation of CO. The CO_2 corresponded to ·313 grms., equal to 12·3 per cent. of carbon on the Fe present.

In this last instance, the higher temperature has materially lessened the carbon deposition, inasmuch, as, although the operation lasted two and a half times as long as the previous trial, the C obtained is a mere fraction above half that in experiment 336.

Believing it improbable that the metallic, spongy Fe should have been instrumental in resolving CO into C and CO_2, without itself suffering some change, the various steps of the process were narrowly watched. In some experiments, after the spongy iron had been exposed to CO for a known time, H was again passed through the tube by means of the arrangements of pinch cocks and T tube, formerly described. In all these cases, there was a formation of H_2O, the oxygen of which could have only come from CO. In other experiments, the CO_2 formed by the action of the CO on the spongy iron was collected and weighed, and the residual carbon was likewise determined. This latter was always in excess of the former, showing that a hypothetical splitting up of 2 CO into C and CO_2 would not alone account for the observed facts. In other instances, again, the tube was allowed to cool in a stream of CO, the residual mass weighed, and the deposited carbon determined; the iron present being known from the weight of the pure Fe_2O_3 used. It was always found that the Fe and C together fell short of the actual weight of the residual substance, showing that it must have contained oxygen in addition.

Exp. 334. 2·448 grammes spongy Fe from Fe_2O_3 reduced by H:—

CO_2, collected during passage of CO for one hour at a very dull red heat	0·214	grammes.
CO_2 produced on combustion of carbonaceous mass in oxygen	·237	„
Difference	·023	„
This represents of carbon	0·006	„
originally associated with, of oxygen	0·008	„

This amount of oxygen must therefore have been taken up by the spongy iron; in confirmation of this, 0·0065 grammes of H_2O were collected, on passing hydrogen a second time over the carbonaceous mass (previous to its combustion in oxygen), corresponding to, of oxygen, 0·006 grammes.

The slight discrepancy between this number and that got before, 0·008, arises from the impossibility of collecting the CO_2 contained in the large excess of CO without slight loss, either from deficient absorption, or from the removal of traces of aqueous vapour from the potash bulbs.

Exp. 335. The residual iron oxide left in the last experiment after burning off the carbon in oxygen was again thoroughly reduced in H, then exposed to CO at a low red heat for 2½ hours.

H_2O produced by second passage of H	0·023	grammes, representing of oxygen ... ...
	0·0204	grammes.
Weight of residual iron and carbon	2·759	„
Do. of iron in 3·497 Fe_2O_3	2·448	„
Leaving for carbon deposited	·311	„
And the carbon, as determined by combustion was	·313	„

Exp. 336. The weight of residual Fe + C + O obtained after reducing the 5·487 grammes, Fe_2O_3, mentioned in experiment 331, and then exposing it to CO for 4½ hours was ... 4·707 grammes.

Fe in 5·487 Fe_2O_3 is	3·841	grammes. ...
C left on solution in H Cl ...	·780	„ 4·621 „
Leaving for O taken up by Fe	·086	„

These last experiments yield the following numbers, calculated upon 100 parts of metallic iron present:—

	A	B	C
Time of exposure to CO ...	1 hour ...	2½ hours ...	4½ hours
Temperature ...	very dull red.	Low red heat.	Melting zinc.
Oxygen in reformed iron oxide ...	0·34 0·24	0·84	... 2·24
Carbon deposited	2·64	12·7—12·8	... 20·3

It would, therefore, seem that the amount of reformed oxide increases with the quantity of deposited carbon. This increase, however, may not be in a perfectly corresponding ratio, owing to the power of CO to reduce the newly-formed oxide, varying at different temperatures. The proportion of oxygen absorbed by the iron for each 100 parts of carbon deposited, is, for—

A	B	C
10	6·6	10

So that as the temperatures at which the operation has been carried on approach each other, as happened in the case of A and C, the ratio between carbon deposited and oxygen absorbed are the same, viz., about 7 equivalents of the former to 1 of the latter, and the

equation would stand thus, provided the oxide of iron were protoxide, which is not certain:—

$$13\,CO + Fe = 7\,C + Fe\,O + 6\,CO_2.$$

As the temperature rises, spongy iron exerts but little action on CO. Precipitated Fe_2O_3, after complete reduction by H, was exposed to a stream of CO, at a bright red heat: after one hour's exposure the composition of the substance was—

Exp. 337. ... ... Fe 99·20 C 0·32 O 0·48, and after 3 hours more ... ... „ 99·34 „ 0·30 „ 0·36.

In such cases as the present, either the CO_2, generated by the splitting up of CO quickly gasifies at high temperatures the deposited carbon directly, or, what is more probable, the acid itself is resolved into CO by yielding O to the metal, and the oxide of iron, so formed, is again reduced by carbon previously precipitated.

The presence of CO_2 in the CO, of course, intensifies the oxidizing influence of the mixtures, and although some carbon may be deposited, the absorption of oxygen predominates.

Exp. 338. A mixture of 100 vol. of CO and 9 vol. of CO_2 was passed over spongy iron for 2½ hours; at the end of this time its composition was—Fe 91·42 C·33 O 8·25=100.

Before leaving the subject of carbon deposition on pure spongy iron, it may be interesting to quote the results of a simultaneous exposure of this substance, and oxides of iron differently prepared in the lead bath arrangement, during a period of nine hours, to a temperature of melting zinc:—

	Substance employed.	C. deposited per 100 Fe present.
Exp. 339.	Pumice-stone, saturated with Fe_2O_3 from $FeSO_4$	808
„ 340.	Precipitated Fe_2O_3 anhyd.	207
„ 341.	Fe_2O_3 from $FeSO_4$	206
„ 342.	Pure, spongy iron	158

So that these figures do not indicate that iron, in its metallic state, possesses any advantage over its oxide in separating C from CO.

To compare the effect produced by heated CO on iron of a porous texture, with that when solid iron was used:—

Exp. 343. Thirty feet of fine iron wire (one foot weighing ·59 grains) was well cleaned with sand paper, cut into short lengths,

and introduced into a half-pound flask provided with a thermometer, and also with outlet and inlet tubes. A rapid stream of CO was driven through the apparatus for one hour, the gas being previously thoroughly purified, by passing through 2 KHO bottles, $AgNO_3$, and KHO bulbs. It showed no turbidity in being passed through lime water for 20 minutes. Heat was now applied by the air bath, and observations made of the issuing gas on lime water.

Time.	Temperature.			Effect on lime water.
1 hr. 0 min.	18° rising to	204°C.	(65° to 400°F.)	nil.
0 „ 30 „	204 do.	227	(400° „ 440°F.)	do.
0 „ 25 „	227 do.	243	(440° „ 470°F.)	do.
0 „ 45 „	243 do.	271	(470° „ 520°F.)	do.
0 „ 30 „	271 do.	282	(520° „ 540°F.)	No opalescence.

So far then as the lime water indicated, there was no action, but next day, on examining the wire, almost the whole was turned blue, and the remainder, straw colour; and when strong HCl was poured upon it, and almost immediately decanted off, the solution gave an intense blue with ferrocyanide of potassium, showing a film of oxide of iron, higher than Fe O, had been formed, and proving that a portion of the CO had been decomposed, but in too minute quantity to produce a perceptible effect on lime water.

Exp. 344. The same wire was next exposed to a higher temperature, viz., bright red, but previously to turning on the CO, H was passed over the wire, in a heated state, to reduce any rust which might be adhering to its surface.

The CO was obtained from sulphuric acid and ferrocyanide, passed through a bottle, containing a solution of potash, then, through two tubes, containing $AgNO_3$; three tubes, containing dry Ka O; and one, containing pumice-stone, saturated with HSO_4. Air was expelled by passing this gas through the apparatus for $1\frac{3}{4}$ hours, heat was then applied and maintained at a bright red for four hours, the current of CO being continued until the whole was cooled.

The wire was blue on the surface, and the 40 grains used had increased ·12 grains.

The potash bulbs behind the apparatus had increased in weight, ·27 grains.

According to the action of $2CO=C+CO_2$, ·27 gr. of carbonic acid collected in the potash bulbs, ought to represent ·07 grains of

deposited carbon, but the gain in weight being ·12 grain, the difference of a portion of it must be due to oxidation of the iron, indications of which were manifested by the change of colour in the wire itself.

The wire, which had served in the experiment, was then dissolved in one portion of HCl, and a similar quantity, which had been exposed to the hydrogen current alone, was similarly treated by another portion of HCl. The solution from the first had floating about in it some whitish flocculent particles, and a few small black flakes. In the second, an extremely minute trace of the whitish matter appeared in two days, but no appearance of the dark coloured flakes could be perceived.

This experiment, therefore justifies the belief that compact iron slowly acts on CO by resolving it into C and CO_2, while the metal, itself, acquires a minute trace of oxygen.

This view of the effect of iron, in its dense form, on oxide of carbon is further confirmed by the appearance of the inside of the iron vessel which served to contain the specimens exposed to the action of CO in the lead bath. It was noticed, after this apparatus had been in use a few times, the interior was coated, uniformly, with an impalpably fine black dust—no doubt, C, precipitated from the CO, to which the surface had been exposed.

Exp. 345. The faculty of metallic iron, particularly in a state of fine division, to precipitate carbon from oxide of carbon, being now proved beyond a doubt, steps were next taken to ascertain its effect upon the gas, at lower temperatures.

All the precautions, previously described, to ensure, as far as practicable, the absolute purity of the CO, were observed, and, as in one or two cases, the $Ag\,NO_3$ was blackened by the passage of the gas, to prevent any CO_2, which might thereby have been generated, the CO, before being admitted to the reduced oxide, was freed from such possible contamination by being passed through two tubes, containing KHO in its solid form, which also retained any moisture, avoiding thus, the introduction of any impurity by the use of SO_4H_2 and pumice-stone. The gas, thus purified, was passed through the apparatus for two hours, before the Liebig's tube, which contained spongy iron, was attached, or heating commenced.

The gas was tested, previous to immersing the tube in the air bath, with the following results :—

5·75 volumes exploded with O gave

	Contraction.		CO_2
	2·90	=	5·80
Theoretical for pure CO ...	2·875	=	5·75

The spongy iron was ascertained to contain 99·9 per cent. of Fe, by permanganate, harpsichord wire being 99·5. After it had been exposed for five and a half hours, at a temperature of 238° to 243°C. (460° to 470°F.), the iron had a black, apparently carbonaceous layer, on the surface, and yielded a distinct quantity of CO_2, on burning in a stream of oxygen. The metal, moreover, had increased in weight 0·3 per cent.

Exp. 346. In order to observe the rate at which CO_2 was given off by pure, spongy iron acting on CO, the KHO bulbs were weighed at various intervals, but, of course, the weights so obtained do not represent the CO_2, generated by the carbon deposition, alone, but also that due to the oxidation of the Fe_x $CO + Fe = Fe\ O_x + xCO_2$.

Thermometer range.		Time of exposure.	Increase of KHO bulbs.
227° to 254°C.	(452° to 470°F.)	... 1 hour ...	·011grammes
232 „ 240	(450 „ 472°F.)	... ¾ „ ...	·009 „
232 „ 240	(450 „ 472°F.)	... 1¾ „ ...	·034 „
232 „ 221	(450 „ 420°F.)	... 1½ „ ...	·017 „
227 „ 238	(452 „ 460°F.)	... 1 „ ...	·008 „
243 „ 238	(469 „ 460°F.)	... 1¼ „ ...	·023 „

The spongy iron had increased in weight, and contained traces of carbon—·009 per cent.

The behaviour of spongy iron when enveloped in the earthy constituents found in an ore, is similar in every respect to the metal when presented in its isolated form to the action of CO, as described in the experiments immediately preceding, only the diluted condition in which the Fe is found, for example in calcined Cleveland ore reduced by H, interferes, as one might expect, with the rapidity of the action.

A quantity of this ore was completely reduced by H, when it was found to consist of :—

Fe	50·58
Earthy matters	49·42
	100

Exp. 347. After 4½ hours' exposure to a current of CO at a temperature of melting zinc, about 420°C. (788F.), its composition was :—

Fe	49·83
Oxygen by difference ...	·07
Earths	48·67
Carbon	1·43=2·87 per 100 Fe.
	100·00

Exp. 348. Three hours' exposure to CO at a red heat gave—

Fe	49·88
Oxygen by difference ...	·20
Earths	48·68
Carbon	1·24=2·48 per 100 Fe.
	100·00

In experiments 245, *et seq.*, it was shown that when the proportion of CO_2 exceeded 50 volumes to 100 of CO, all carbon deposition was suspended when oxide of iron, in various ores, was exposed at different temperatures to such a mixture. The same law holds good when the iron contained in such ores has been previously reduced to the metallic condition by hydrogen, oxidation of the Fe taking place. This circumstance appears to prevent carbon impregnation.

Subject to all the precautions of excluding air, and avoiding other circumstances which could interfere with the results, the following trials were made with perfectly reduced Cleveland ore :—

	Mixture of gas. CO.	Mixture of gas. CO_2	Time of exposure.	Temperature.	Carbon deposited.	Oxygen absorbed per 100 of Fe
Exp. 349.	100 vols.	616 vols.	¾ hr.	melting zinc	nil	18·46
„ 350.	„	98	½	do.	„	0·0
„ 351.	„	„	½	bright red	„	5·91
„ 352.	„	61	13½	do.	„	3·48
„ 353.	„	57	7	do.	„	5·14
„ 354.	„	38	½	melting zinc	„	1·31

The deposition of carbon from CO, as it is effected by metallic iron is, it has been proved, always accompanied by the simultaneous oxidation of a minute portion of the Fe, it remains to be considered, whether, when the metal is taken in its oxidized state, any carbon impregnation takes place before a minute quantity of iron is brought down to the condition of Fe, a state of things deemed indispensable, I believe, by previous writers. It is obvious, that if a mere absorption of O is required, a lower state of oxidation, passing into one of a higher description, may suffice, and thus iron, in its metallic form, may not be required.

To ascertain whether there was any metallic iron present, the iodine test, examined in experiment 51, *et seq.*, was employed, in which, it will be remembered, that although it was impracticable to distinguish whether iron, as hydrated Fe O or Fe, is present in the substance in question, it was easy to say whether the metal in neither of these conditions existed; moreover, anhydrous protoxide was almost unaffected by iodine and cold water. Under these circumstances, then, we may speak confidently, that when iodine and cold water dissolves no iron, neither hydrous Fe O, nor Fe are present, and the anhydrous protoxide, if present, must be so in very small quantities.

The following trials illustrate the change experienced by different oxides of iron, exposed simultaneously for seven hours in the lead bath, to the action of CO, zinc melting, but antimony not:—

Substance used.	Exp. 355. Fe_2O_3 from $FeSO_4$	Exp. 356. Precipitated Fe_2O_3	Exp. 357. Fe O from Nitrate.	Exp. 358. Pumice and Fe_2O_3	Exp. 359 Calcd. Clev. ore.
Carbon	31·9	45·5	56·3	1·69	0·11
Fe, soluble in iodine	11·4	2·5	1·4	nil	nil
Fe, insol. in do.	47·1	45·2	37·7	11·34	40·60
O by difference...	9·6	6·8	4·6	3·71	15·75
Earthy matter ...				83·26	43·54
	100	100	100	100	100

Calculated upon 100 parts of metallic iron present, the above numbers yield:—

	Fe_2O_3 from $FeSO_4$	Precipitated Fe_2O_3	Fe_2O_3 from Nitrate.	Fe_2O_3 Pumice-stone	Calcd. Clev. ore.
Fe soluble in iodine	19·5	5·3	3·7	0·	0·
Carbon	54·5	95·4	144·0	14·9	0·3
Oxygen	16·4	14·3	11·7	32·7	38·8
Perct. original O lost	61·7	66·6	72·4	23·6	3·2

These numbers show how materially the molecular state affects deoxidation and carbon deposition, and, at the same time, they prove that the extent of the latter is firstly independent of the presence of any metallic iron (*vide* experiment 358), and, secondly, that it bears, as usual, no ratio to the extent to which the oxygen has been removed, although in each of these cases where the loss of oxygen has been the largest, the carbon deposited is the highest.

The view of the deposition of carbon being effected without the necessary formation of any metallic iron, was also borne out by the following experiment:—

Exp. 360. Well calcined Cleveland ironstone was exposed for 3½ hours to the action of CO, freed from any traces of free oxygen, and from carbonic acid by passing through strong alkaline pyrogallate solutions. The temperature was close on that of melting zinc, and the CO_2 produced, and C deposited, were estimated.

The ore lost ... ... 2·55 per cent of its weight.
CO_2 collected, equal to ... 13·00 of weight of ore.

Residual carbon, estimated by solution in HCl, collected in asbestos filter, and combustion with lead chromate=0·90 per cent., or 2·3 per 100 of metallic iron present:

Hence, loss of weight ... ... = 2·55 per cent.
Carbon deposited ... ... = ·90 „
Oxygen removed ... ... = 3·45 „

Again: oxygen, corresponding to 13·0 CO_2 collected = 4·72
do. associated with ·90 C deposited = 1·20
Difference = oxygen removed ... = 3·52

The agreement between these determinations shows the experiment to be trustworthy. On solution of the residual substance in HCl, and titration with permanganate, a quantity of ferrous

compound was found equivalent to 23·2 per cent. of Fe, or 29·8 of Fe O.

If the reduction had been from $Fe_2 O_3$ to 2 Fe O, this amount of protoxide would have generated, by the removal of—

$$\frac{16}{144} \times 29{\cdot}8 = 3{\cdot}31 \text{ per cent. of oxygen,}$$

whilst, had metallic iron been formed to this extent, an amount of oxygen must have been removed equal to

$$\frac{3 \times 16}{144} \times 29{\cdot}8, \text{ or } 9{\cdot}93 \text{ per cent. of O.}$$

The actual amount removed being close upon the former number, it appears that no appreciable quantity of metallic iron could have been produced.

In no instance, let it be remembered, was it found practicable to remove the whole of the oxygen contained in the iron oxide employed by pure CO at temperatures short of a dull red heat, after 12 or 14 hours' exposure, even when the carbon greatly exceeded the weight of iron present. The curious fact, however, was noticed, that when the greater part of the oxygen was removed, the amount of iron insoluble in iodine and cold water, after some hours digestion, was considerably more than that corresponding to the formula Fe O, thus apparently indicating the formation of some sub-oxide, in the way already described. The three varieties of pure $Fe_2 O_3$ previously employed yielded the following results, the temperature being about that of melting zinc, or a little higher:—

	Exp. 361.	Exp. 362.	Exp. 363.	Exp. 364.	Exp. 365.	Exp. 366.	Ex. 367.
Substance used—	Precipitated Fe_2O_3 anhydrous.			Fe_2O_3 from $FeSO_4$	Fe_2O_3 from nitrate.		
Time of exposure,	7½ hours	7 hrs.	10 hrs.	15 hrs.	7 hrs.	7 hrs.	7½ hrs.
Iron insol. in I.	33·1	45·2	51·20	28·0	47·1	37·7	45·9
Do. sol. ,,	Nil.	2·5	·10	·6	11·4	1·4	Nil.
Carbon	58·7	45·5	35·85	64·4	31·9	56·3	46·1
Oxygen	8·2	6·8	12·85	7·0	9·6	4·6	8·0
	100·	100·	100·	100·	100·	100·	100·
Oxygen remaining with 100 parts iron insoluble in iodine	24·8	15·0	25·1	25·0	20·4	12·2	17·4
Carbon per 100 of Fe present	177·3	95·3	69·5	225·1	54·5	144·0	100·4

Theoretical oxygen for 100 of iron being for $Fe_2 O$ ... 14·3

$Fe O$ ... ... 28·6

$Fe_2 O_3$ ... 42·8

Similar results were obtained on exposing various ores of iron to the action of CO in the lead bath apparatus. In all cases, the ores were previously heated in a muffle, to secure complete dryness and peroxidation.

	Exp. 368.	Exp. 369.
Substance used	Clev. calcd. ore.	Hæmatite Lancashire.
Time exposed	7 hours.	7½ hours.
Temperature	Melting zinc in both cases.	
Composition after exposure, as determined by analysis	Fe sol. in I, nil.	0·20
	Fe insol. „ 40·6	33·35
	Oxygen ... 15·75	9·05
	Carbon ... ·11	22·10
	Earths ... 43·54	35·30
	100·00	100·00
Oxygen remaining with—		
100 parts Fe insoluble in I	38·8	27·1

SECTION XV.—PROBABLE NATURE OF CHANGE IN CO AND IRON OXIDES IN THE DISSOCIATION OF CO.

The conclusion to be drawn from all these experiments is, that the reducing agent must have been a lower oxide of iron, and that the action was of this nature—

$$Fe_xO_y + z\,CO = z\,C + Fe_x\,O_{y+z}$$

and further, that it is probable that x is greater than y, *i.e.*, that some sub-oxide produced by the action of CO on Fe_2O_3.

It may further be inferred that when the action of CO on Fe_2O_3 has gone on for some time, there is produced a mixture of

Metallic iron.
Unknown oxide of iron $Fe_x\,O_y$ and
Carbon,

and that there is a tendency towards each of the following reactions :—

A. Action of CO on $Fe_x\,O_y$ producing CO_2 and some lower oxide.

B. Reaction of this lower oxide on CO reproducing $Fe_x\,O_y$ and setting free carbon.

C. Action of carbon on $Fe_x O_y$ forming metal and lower oxide along with CO, and CO_2.

D. Action of metallic iron on CO, reproducing $Fe_x O_y$, or lower oxide, and setting free carbon.

E. Action of CO_2, set free in above reactions upon carbon, metallic iron, and lower oxide of iron.

It appears therefore highly probable, as has been already stated, that under certain circumstances, the above five tendencies may balance each other, so as ultimately to yield a substance, upon which CO is absolutely inert.

The composition attained, when such is the case, will manifestly depend on the temperature, and probably on the molecular condition of the $Fe_2 O_3$ employed in the first instance.

The fact that no experiments were successful in obtaining substances free from O by the action of CO on $Fe_2 O_3$, at temperatures close on that of melting zinc, seems to indicate, that at this temperature the oxidizing action of CO and CO_2, jointly on Fe, was approximately equal to the reducing action of C and CO on the the $Fe_x O_y$ present, but the large increase in quantity, of deposited carbon on a rëexposure of one specimen to the action of CO (experiment 207), appears to indicate, that at this temperature, the tendencies towards carbon deposition are more powerful than those towards carbon gasifaction.

At a bright red heat, a different state of things obtained, pure $Fe_2 O_3$ (precipitated) was wholly reduced by the hydrogen, as in former experiments, and exposed to the action of CO at the above named temperature, and the original $Fe_2 O_3$ was also exposed similarly, with the results annexed:—

Exp. 370. $Fe_2 O_3$—exposure 5 hours to CO at bright red heat: Composition of residue, Fe, 99·33; O, 0·43; C, 0·24 = 100.

Exp. 371. $Fe_2 O_3$, reduced by H, exposed to CO, at bright red heat for one hour: Composition became Fe, 99·20: O, 0·48; C, 0·32; = 100.

Exp. 372. $Fe_2 O_3$, reduced by H, similarly exposed for four hours: Composition of residue, Fe, 99·34; O, 0·30; C, 0·36 = 100.

Hence, it appears, that a position of equilibrium, among all the above five tendencies, has been arrived at, the composition of the inert substances, at this temperature, being virtually the same in the three cases.

The small quantity of carbon in the mixture, shows, how energetic is the action of this substance on the oxide $Fe_x O_y$, the deposited carbon being gasified, almost as quickly as formed, and these results corresponded entirely with those obtained when Cleveland calcined ore was used, the gasifying tendencies rising with the temperature, as exhibited in experiments 211, 287, 228, and 229, in which the carbon deposited was per 100 of iron present,

At a temperature not visibly red, in 4½ hours ...	64·0
Temperature, bordering in redness, 4½ hours ...	57·6
do. red hot 11 hrs., bright red 10 hrs., in all, 21 hrs.	2·3
do. very bright red ... ... 4½ „	0·3

SECTION XVI.—HEAT ALONE DOES NOT SUFFICE FOR DISSOCIATING CO. IN THE BLAST FURNACE.

The carbonic oxide generated in the hearth of a blast furnace meets with several substances which, although in a highly heated state might, without even the test of direct experiment, be regarded as inert in decomposing this gas. These are chiefly silica, lime, and alumina.

Mr. St. Claire Deville had, it is true, succeeded in separating carbon from carbonic oxide by the mere application of heat, but this was done by instantly cooling the precipitated carbon below the point where reoxidation was possible.

This is a condition, however, which could never obtain in a blast furnace, but being unwilling to take any thing for granted, without direct proof, the following trials were made:—

Exp. 373. Pure CO, carefully freed from HCy was passed during eleven hours through a tube filled with asbestos kept at a red heat. Not a trace of C was deposited.

Exp. 374. The same experiment was repeated with CO still retaining a trace of H Cy vapour. A minute quantity of carbonaceous substance was deposited after twenty-one hours exposure, representing 0·004 quammes of carbon (burnt in oxygen).

Exp. 375. Carbonic oxide from ferrocyanide of potassium purified by KHO and $Ag NO_3$ and dried by means of $Ca Cl_2$ was passed through twelve inches of pumice stone for two hours, kept at a

red heat in a porcelain tube, the pumice stone having been previously exposed to a high temperature without loss of weight. A tube containing Ca Cl_2 received the gas after its passage through the pumice showed an increase of 0·3 grain, and potash-bulbs beyond it,also with a Ca Cl_2 tube, gained 0·6 grain in weight.

I was induced to repeat experiments because Gmelin, in his handbook of Chemistry, mentions that CO is decomposed by passing it through a red-hot tube.*

SECTION XVII.—EFFECT OF CERTAIN METALLIC SUBSTANCES BESIDES IRON ON CARBONIC OXIDE, INCLUDING SILICON.

A dense fume is emitted from furnaces smelting the Cleveland iron stone, and this condensing, lodges in large quantities in the pipes for conducting the gases to the boilers, &c. In the so-called flue-dust, zinc is always found, and in most ores there is more or less manganese, occasionally copper, often titanium, and some other metals.

Under the circumstances, it was natural to try the power of metals thus often found associated with iron in its ores, in splitting up CO, to which was added experiments upon others not generally found in connection with that one which it is our more immediate province to examine.

In the following experiments, every care was taken to have the CO free from Cyanogen, otherwise, a carbonaceous deposit, probably paracyanogen, takes place, and to have the metals and their oxides without a trace of iron. In one case, that of copper, in the first trials a minute quantity of carbon was found deposited, which subsequent investigation proved to be caused by a trace of iron being present.

Manganese—

Dioxide ($Mn O_2$) was obtained by boiling an alkaline permanganate with nitric acid, and drying the precipitate after it was thoroughly washed.

Manganoso manganic oxide ($Mn_3 O_4$) was got by heating pure $Mn CO_3$ in a current of air until it contained no trace of CO_2.

* Translation by Cavendish Society, Vol. II., p. 89.

The Mn CO_3 was procured free from iron by adding a small quantity of $Na_2 CO_3$ to a solution of manganese, and boiling the resulting turbid liquor until every trace of iron was precipitated by the Mn CO_3 thrown down at first. The filtered liquid thus freed from Fe was then precipitated by further addition of $Na_2 CO_3$ and the precipitate thoroughly washed and dried.

These two oxides were exposed to a stream of pure CO with the results given below.

	Exp. 376. Mn O_2	Exp. 377. Mn O_2	Exp. 378. $Mn_3 O_4$
Time of exposure: ...	4½ hours ...	6½ hours ...	10 hours
Temperature: ...	Below red heat	Zinc softened	Zn fused, Sb not.
Loss of weight ...		... 19·6 per ct.	7·1 per ct.
Theoretical loss for reduction to Mn O ...		... 18·4 „	7·0 „
Increase of weight on roasting in oxygen ...	7·53 pr. ct.		
Theoretical increase of weight for $Mn_3 O_4$ ...	7·51 „		
Carbon deposited ...	nil ...	nil ...	nil

From these trials, it seems that Mn O_2, at a heat short of redness, is converted by CO into Mn O in 4½ hours, and that both Mn O_2 and $Mn_3 O_4$ lose oxygen readily at the temperature of melting zinc, both being reduced to Mn O.

In no case was there a trace of carbon present. It would therefore appear that oxides of Mn are incapable of acting on CO, as Fe does, by separating this gas into C and CO_2, and that no suboxide $Mn_2 O$ is formed.

Copper—

Pure copper oxide was got by electrolysis of recrystallized sulphate, solution in nitric acid, evaporation, and ignition.

Exp. 379. The oxide of copper was exposed at a temperature of melting zinc to CO for 7 hours, after which its composition was—

Copper	98·1
Oxygen	1·9
C	nil
	—— 100

So that reduction was nearly complete in this time.

Exp. 380. At a low red heat, oxalic acid gas (equal vols. CO and CO_2) withdrew all the oxygen from oxide of copper. The loss

of weight was 20·3 per cent—20·2 per cent. being the theoretical equivalent of O. No carbon was precipitated.

Exp. 381. Pure spongy Cu, obtained by reducing the above oxide in H, was kept in contact with CO for 10 hours, at a temperature of melting zinc :—No change of weight, hence no C deposited.

Exp. 382. Pure spongy Cu, exposed for 2 hours to oxalic acid gas, at a dull red heat, did not alter in weight.

Zinc—

Zn O was obtained by treating pure Zn Cl_2 with Na_2CO_3, and igniting the Zn CO_3 obtained :—

Exp. 383. Exposed at temperature of melting zinc to pure CO for 6½ hours. No carbon deposited, nor was there any sensible amount of reduction, the weight of the product not being altered by moistening with NO_3H and gentle ignition.

Tin—

Stannic oxide obtained by oxidation of block tin by nitric acid.

Exp. 384. Action same as with Zn O in CO, at temperature of melting zinc. No carbon, nor any appreciable amount of reduction, the weight not altering sensibly by treatment with NO_3H.

Chromium—

Exp. 385. Anhydrous chromic oxide obtained by igniting potassium, anhydro-chromate (bichromate of potash), and washing the product.—Had become darker, but contained no carbon, and was in other respects unchanged by exposure to CO for 7½ hours, in lead bath, to about 410°C (770°F.)

Exp. 386. Hydrated chromic oxide, got by precipitation of chloride by means of ammonia, was exposed at the same time as the chromic oxide in previous experiment.—Original colour, bluish green, changed to bright green. In other respects, no change, save that almost the whole of the water of hydration was expelled.

Lead—

Lead oxide got by ignition of crystallized nitrate :—

Exp. 387. Pb O exposed to CO, for 6½ hours, at a temperature of melting zinc.—Perfect reduction ensued.

Exp. 388. Pb O, same treatment and same results, at red heat, in 6½ hours.—No trace of carbon in either of these experiments.

Nickel—

Recrystallized nickel nitrate (commercially pure) was boiled with nitric acid, and an excess of ammonia added. This dissolved the precipitated oxide of nickel, but left a trace of Fe_2O_3, which was separated in the usual way. The alkaline solution of the oxide of nickel was evaporated to dryness, and ignited in two portions. Either from the presence of a little adhering nitrate of ammonia, or from differences in the temperature at which ignition was effected, two different oxides were obtained—the one, compact, and nearly corresponding to Ni O (Ni 78·7 O 21·3); and the other, to Ni_2O_3 (Ni 71·1 O 28·9).

The two oxides of nickel thus obtained had the following composition, arrived at by reducing known weights of each in pure hydrogen.

	Compact Oxide.	Black Oxide.
Ni ...	77·5 ...	71·2
O ...	22·5 ...	28·8
	—— 100	—— 100

These two substances were exposed to a current of pure CO in the lead bath arrangement:—

	Exp. 389. Compact oxide. Time of exposure—7½ hours. Temperature—Zinc melted.—Antimony not affected.	Exp. 390. Black oxide. Time of exposure—10 hours. Temperature—Zinc melted.—Sb not.
Composition of Product. Ni	87·2	28·1
O	12·2	
C	0·6	71·9
	100·	100·

In experiment 389, the residual oxygen is just 14·0 per cent. of the weight of the total nickel present: this represents an oxide, having almost exactly the composition of Ni_2O (which requires 13·6 to 100 Ni). No nickel, in this case, was dissolved out by iodine; and as iodine was found to attack spongy nickel reduced by hydrogen, with ease, there could have been no metallic nickel present.

It was shown formerly (experiments 62 to 69), that in several instances where F_2O_3 had been imperfectly reduced by CO, the proportion between the iron insoluble in iodine, and the residual oxygen, was almost exactly that required to form a suboxide, F_2O: hence, it would appear, that nickel and iron are analogous in this respect also, viz., that the suboxides of both are

not acted on by iodine and cold water. As will be presently shown, Co_2 O, if formed, is acted on thus, the product being, however, not the sesquioxide (as in the case of iron when the hydrated protoxide is thus oxidized), but the protoxide.

In the case of the Ni_2 O_3, the carbon and oxygen determinations were faulty, and the sum of both was ascertained by finding the quantity of nickel present in the mass after exposure to CO. The result is such that there must have been a carbon deposition equal to about 250 per cent. of the nickel actually present.

In a stream of oxalic acid gas (equal volumes of CO and CO_2), the compact oxide gave the following results:—

				Per cent.
Exp. 391.	O lost in	2½ hours	... at a low red heat ...	20·4
	do.	3 „	more do. ...	1·1
	do.	3 „	„ do. ...	·2
		8½		21·7
Exp. 392.	O lost in	3 hours	at a bright red heat ...	22·
	do.	2 „	more do.	0·1
		5		22·1

The original oxygen present being 22·5 per cent., it appears that a mixture of equivalents of CO and CO_2 has the power, at both these temperatures, almost completely to deoxidize Ni O.

Trials were then made to discover the action of the pure spongy metal on pure CO. A portion of the compact oxide was reduced in hydrogen until no more H_2 O was evolved. A current of CO was then passed over the metallic Ni thus obtained:—

Time of exposure		Exp. 393.	5 hrs.		Exp. 394.	5 hrs.
Temperature ...		Melting zinc	... ...		Bright red heat	
Composition of Product.	Ni	...	99·93	... ...	100·	
	C	...	·04	... ...	·0	
	O	...	·03	... ...	·0	
			100·		100·	

The dissociation, therefore, of the CO at a temperature of melting zinc was very feeble, and at a bright red heat it was nil.

The power of the spongy metal to decompose CO_2 was next made the subject of investigation.

Exp. 395. At melting zinc, no appreciable amount of CO was obtained after 30 minutes' exposure—the metal gaining in weight, 0·3 per cent.—probably due to traces of moisture and air present.

Exp. 396. At a low red heat, the metal gained 3 per cent. of its weight in 90 minutes.

Exp. 397. At a bright red heat, 40 ccs of gas were obtained after 40 minutes' exposure, which was unabsorbed by potash. It was found to contain 96 per cent. of CO.

Exp. 398. Spongy nickel, at a moderately bright red heat, was unaffected after an exposure of 15 hours to oxalic acid gas (equal vols of CO and CO_2.)

The nickel oxide employed in these experiments might contain some cobalt, but if so, it was the minutest trace; not the faintest indication of its presence being indicated by the very delicate test afforded by the borax bead before the blow-pipe.

Cobalt.—

A cobalt oxide was prepared from the purified nitrate in the same way as the oxides of nickel above described.

It was almost pure $Co_3 O_4$ (Co 73·5 O 26·5), its composition being

Co 73·3
O 26·7

A small trace of Ni might be present, but if so, it could not materially affect the result, inasmuch as Co O is much more powerful in splitting up CO than is Ni O.

Specimens of this oxide of cobalt ($Co_3 O_4$), were exposed in the lead bath arrangement.

		Exp. 399.			Exp. 400.	
		Time of exposure 7½ hours.			10 hours.	
		Temperature. Zn. fused.	Sb not.		Zn fused.	Sb not.
Composition of product ...	Co soluble in I...	47·2	...	...	17·3	
	Co insoluble „ ...		...	...	20·4	
	Carbon	46·4	...	...	56·8	
	Oxygen...	6·4	...	...	5·5	
		100·			100·	

The condition in which the cobalt exists was not determined, *i.e.*, whether part as metal and part as oxide, or whether the whole was a suboxide. In experiment 399, the oxygen per 100 of total cobalt present was 13·56, and in experiment 400 14·58, which correspond

nearly with Co_2O (100 Co 13·6 O). It was ascertained that the anhydrous Co_3O_4 used was attacked by iodine and water, so that it was not possible by the use of this reagent, as in the case of iron and nickel, to distinguish between metallic cobalt and its oxide. The oxygen in experiment 400 existed to the extent of 27·0 per 100 parts of that cobalt which was found to be insoluble in iodine and cold water, which indicates that the action of iodine on the Co_2O probably formed gives rise to Co O, and not Co_2O_3; the former formula requiring 27·1 of O per 100 of Co, thus:—

$$Co_2O + I_2 = Co\,I_2 + Co\,O,$$

which indicates a double difference between the behaviour of the lower oxides of Co and Fe under these circumstances. The fact that the Co_3O_4 originally used was attacked by iodine, however, probably indicates that Co O_3 is producible by the action of iodine on the lower oxides; a reaction probable, *a priori* from the well-known formation of Co_2O_3 from the action of chlorine on alkalised solutions of cobalt.

The presence of CO_2, to the extent of an equal volume, does not prevent CO from completely reducing the cobalt oxide under examination (Co_3O_4.)

Exp. 401. Temp. dull red.	Exp. 402. Temp. bright red.
O lost in 2½ hours 26·5 per cent.	O lost in 3 hours 26·6 per cent.
3 „ more ·1 „	
26·6 „	

the original oxygen being 26·7 per cent.

The effect of cobalt in its metallic state was next tried on pure CO, the Co being obtained by acting on Co_3O_4 by H, until no more H_2O was formed.

	Exp. 403.		Exp. 404.
	Time of exposure—5 hours.		4½ hours.
Temperature ...	Melting zinc		Low red heat.
Composition of Product.	Co ... 98·3	...	99·7
	C ... 1·4	...	0·1
	O ... ·3	...	0·2
	100·0		100·0

To ascertain the power of the spongy metallic cobalt to withdraw O from CO_2, in—

Exp. 405. 120 ccs of gas unabsorbed by Ka HO was collected by passing CO_2 over Co at a bright red heat for 35 minutes. The 120 ccs so obtained contained 96 per cent. of CO.

Platinum—

Although there was little probability of a metal having so feeble an affinity for oxygen as platinum to exert any power of splitting up CO, the following experiments were performed, under the idea that possibly the dissociation of CO by heat alone (which experiment 373 *et seq.*, show does not readily take place), might be assisted by the occlusion of that gas in the pores of a spongy substance gifted with high absorbing powers for gases.

This metal was obtained in its spongy condition,

(A) by ignition of ammonium chloroplatinate:
(B) „ potassium chloroplatinate and washing product.

Exp. 406.	Spongy platinum	(A),	inert, at	melting zinc.
„ 407.	do.	„	do.	low red heat.
„ 408.	do.	(B),	do.	melting zinc.
„ 409.	do.	„	do.	low red heat.

In one of these cases there was a trace of carbonaceous matter deposited, due probably, to the presence of hydrocyanic acid vapour in the CO employed, as the gas used was not wholly freed from this impurity.

Silicon—

Exp. 410. A specimen of this element, in its graphitoidal form, weighing 1·405 grammes, dried at 100°C. (212°F.) lost ... ·005
Just ignited, and lamp removed ... ... „ ... ·013

„ ... 0·018

Then, heated to redness, for half an hour, it gained ... ·006
do. do. more „ ... ... ·004

·010

The substance then contained some body, probably carbon, which exposure to air at a red heat removed, and some modification of silicon, oxidizable at this temperature.

The 1·397 grammes of silicon, remaining after this treatment,

were exposed to a stream of pure CO, for 6½ hours, at a temperature a little above that of melting zinc :—

No change in weight.

Exp. 411. The same specimen was then exposed to CO, at a bright red, for a period of 6 hours, precautions, before and after the experiment, in both cases, being observed to exclude atmospheric air :—

The gain in weight, was ... ... ·18 per cent.
Burnt in oxygen ; gain on original substance, was ... ·29 „
CO_2 collected = ·008 grammes, equal to C ... ·15 „

Looking at the previous behaviour of this specimen of graphitoidal silicon, it is doubtful whether this small quantity of C is owing to carbon deposition, but may rather be due to trace of C or graphite, in the silicon itself.

Titanic acid—

Exp. 412. Cubical crystals of nitride of titanium are commonly found in the hearths of extinguished blast furnaces. The specimen of amorphous $Ti O_2$ employed, was obtained by igniting ammonium titanate : ·464 grammes were exposed for 6½ hours, to a temperature a little above that of melting zinc. The $Ti O_2$ was faintly blackened on its surface :—

The gain in weight, was ... ... 1·2 per cent.
Burnt in oxyogen, it lost again ... ... 1·0 „
CO_2 collected ·019 = C on original $Ti O_2$ ... 1·1 „

Exp. 413. The specimen of $Ti O_2$, freed from carbon by ignition in O, would consist of—

Ti	...	·283
O	...	·181
		·464 grammes.

It was exposed to a bright red heat, for 6 hours, to a stream of pure CO. It was ascertained, by combustion in oxygen, collection of CO_2, and difference of weight, to be now composed of—

Ti	...	·283
C	...	·004
O	...	·1725
		·4595

From these numbers, it appears that the $Ti O_2$ has lost 4·7 per cent. of its oxygen, and deposited carbon, to the extent of 0·9 per cent. of the $Ti O_2$ used, or, 1·19 per cent. on the metallic Ti present.

SECTION XVIII.—SUMMARY OF ACTION OF CO AND CO_2 ON METALS AND THEIR OXIDES, INCLUDING SILICON.

The preceding experiments on the action of CO and CO_2 on metals and some of their oxides, may be summarized as follows:—

ACTION OF CO ON METALS, INCLUDING SILICON.

Iron.—Oxidation of the spongy metal, and simultaneous deposition of carbon take place at all temperatures between 243°C. (470°F.) and a bright red heat. The temperature most favourable to this double action is about that of melting zinc.

Nickel and *Cobalt* are oxidized, and carbon deposited at all temperatures between melting zinc and low red heat, but to a much less extent than happens with iron.

Copper, *Platinum*, and *Silicon* are probably absolutely inert at all temperatures.

ACTION OF CO ON OXIDES.

Iron.—Fe_2O_3—At all temperatures between 150°C. (302°F.) and a bright red heat, deoxidation takes place, but this is never absolutely complete. Both deoxidation and carbon deposition are at a maximum at about the temperature of melting zinc 417°C. (783°F.), but both are materially influenced by the molecular condition of the oxide used, and it would appear also by the rapidity of the current of CO. When deoxidation has taken place to a certain extent, CO appears powerless to remove the remaining oxygen; but a portion of this remnant—the quantity varying with the temperature—may be abstracted by the action of the carbon deposited, this action being perceptible at all temperatures above 249°C. (480°F.), and becoming more intense as the temperature rises. Even at a bright red heat, however, no iron was obtained free from O and C; the joint action of CO and deposited carbon being apparently unable to remove the last traces of oxygen at all temperatures short of absolute fusion. Indeed, this could not be otherwise, seeing that spongy iron itself acquires carbon, and at the same time suffers slight oxidation at this temperature (*vide* experiments 284 to 286.) Previously to the production of metallic iron by this means, a suboxide Fe_2O appears to be formed.

At temperatures between a low red and a bright red heat, a position of equilibrium appears to subsist among the mutual actions of metallic iron, carbonic oxide, deposited carbon, iron oxide, and nascent carbonic acid; but at melting zinc these actions which tend towards carbon deposition overbalance those towards carbon gasifaction, whilst the oxidizing and deoxidizing tendencies arrive and remain at a condition of equilibrium.

Nickel Ni O and $Ni_2 O_3$. At temperatures close on that of melting zinc, the action of CO is similar to that on $Fe_2 O_3$, viz., it only partially reduces the oxides of nickel, the reduction being accompanied by carbon deposition, a suboxide $Ni_2 O$ being probably formed.

Cobalt.—Partial reduction and deposition of carbon also happens when $Co_3 O_4$ is exposed to CO at the temperature of melting zinc, and very probably a suboxide $Co_2 O$ is produced.

The information gained by the change effected by CO on the oxides of nickel and cobalt seems to justify the conclusion that these substances, as well as oxide of iron, are reduced to the metallic state by being first brought to the condition of a suboxide (probably $Fe_2 O$, $Co_2 O$, $Ni_2 O$), the actual production of metal being due to the action of deposited carbon on this suboxide. There are good grounds for such an inference at temperatures near that of melting zinc, and the fact, that at higher temperatures oxygen is always taken up when pure metal is exposed to the action of CO, points to the supposition that this gas cannot meet Fe, Co, and Ni, without being partially resolved into C and O.

Titanium as $Ti O_2$, apparently becomes slightly impregnated with carbon.

Copper and *Lead* oxides experience reduction, almost perfect, at temperatures ranging from melting zinc to red heat, but unaccompanied by a trace of carbon deposition.

Manganese, as $M_3 O_4$ and $Mn O_2$, exposed to CO under a red heat, are reduced to Mn O, the action being unaccompanied by any carbon impregnation.

Zinc, Tin, Chromium, and *Silicon*, as Zn O, $Sn O_2$, $Cr_2 O_3$, and $Si O_2$ are neither reduced at the heat of melting zinc, nor is there any carbon precipitated from the CO.

ACTION OF CO_2 ON METALS.

Iron.—Dry CO_2 has no action on spongy iron at 299°C. (570°F.)

At melting zinc, oxidation is very perceptible, commencing at something between this temperature and 299°C.

Experiments 75 to 80 may be referred to as evidences of the oxidizing action of CO_2 on Fe, increasing very rapidly as the temperature rises.

Cobalt.—A low red heat is not enough to enable this metal to split up CO_2 but the decomposition is perceptible at bright redness.

Nickel.—Much less energetic in splitting up CO_2 into CO than cobalt.

At a bright red heat, the approximate relative action of dry CO_2 on iron, cobalt, and nickel, are :—

Iron—as unity	1
Cobalt	·44
Nickel	·11

These numbers being the relative quantities of CO obtained by exposure of equal weight of the three metals to dry CO_2 under precisely similar conditions.

ACTION OF MIXTURES OF CO AND CO_2

Iron.—Apparently, a position of equilibrium among tendencies towards oxidizing and deoxidizing, carbon depositing, and carbon gasifying, exists, which changes with each temperature, and with the molecular condition of the substance employed, and with the relative amounts of CO and CO_2.

When a mixture of equal volumes of these gases is employed, no carbon is deposited, but with 3 of CO and 1 of CO_2, carbon is precipitated. The actual point where CO is split up into C and O, is somewhere between these two sets of figures. With equal volumes of CO and CO_2, at a bright red heat, metallic iron oxidizes, and ferric oxide reduces to a substance approximating in composition to Fe O, containing no iron in a metallic state, and no carbon.

Cobalt and *Nickel.*—At a bright red heat, a mixture of equal vols. CO and CO_2 almost perfectly reduces the oxides of these metals, but has no perceptible action on the metals themselves. No carbon is deposited in any case.

The following experiments were performed to ascertain what amount of CO_2 would arrest deposition of carbon in oxides of iron, nickel, and cobalt—performed simultaneously in the lead bath apparatus.

The first trial was with a mixture of 50 vols. CO_2 to 100 CO.

	After exposure 5 hours, temperature—zinc soft.						Dull red, 5 hrs.	
	Exp. 414.	Exp. 415.	Exp. 416.	Exp. 417.	Exp. 418.	Exp. 419.	Exp. 420.	Exp. 421
	Clev. Cal. Ore.	Fe_2O_3 precip.	Fe_2O_3 frm $FeSO_4$	Fe_2O_3 frm Nit.	Oxide Nickel.	Oxide Cobalt.	Clev. ore.	Fe_2O_3 Precip.
Per cent. original O removed	2·10	6·8	7·9	5·6	27·9	87·6	13·5	45·8
Carbon deposited per 100 metal.	Nil.	Nil.	Nil.	Nil.	Nil.	14·6	1·3	1·5

The above were submitted to five hours' longer exposure; same temperature.

	Zinc softened.					
	Exp. 422.	Exp. 423.	Exp. 424.	Exp. 425.	Exp. 426.	Exp. 427.
Total percentage of original O lost	10·0	32·8	11·0	37·7	81·0	88·9
Total carb. per 100 of metal.	Nil.	1·2	trace.	8·7	Nil.	28·5

To 100 vols. of CO, 31 of CO_2 were added, and passed over the following substances:—

	In lead bath—5 hours, zinc softened.					Dull red, 5 hrs.	
	Exp. 428.	Exp. 429.	Exp. 430.	Exp. 431.	Exp. 432.	Exp. 433.	Exp. 434.
	Cal. Clev.	Raw Clev.	Precip. Spongy Fe.	Nickel.	Cobalt.	Cal. Clev.	Fe_2O_3 precip.
Original O removed per cent	4·4	...	...	45·2	81 6	68·4	90·0
O absorbed per cent. of that required to form Fe_2O_3	...	...	14·0	...	...	...	...
Carbon per 100 Fe	Nil.	Trace.	Nil.	Nil.	81·2	1·5	0·9

The above were exposed for 5 hours more: temperature—zinc soft.

	Exp. 435.	Exp. 436.	Exp. 437.	Exp. 438.	Exp. 439.
Total per cent. of O removed	6·9	...	...	68·3	91·8
Total carbon per 100 Fe	Nil.	Trace.	Nil.	1·9	154·3
O absorbed	...	...	7·1	...	

The cause of the diminution in the amount of oxygen taken up by the metallic iron is probably the following:—In the first experiment (Nos. 428 to 432) the CO_2 present was increased above the original 31 per 100 of CO by that set free from the raw Cleveland ore, as well as by that produced by the reduction of the substances exposed (which would, further, reduce the quantity of CO present); while, in the second case (experiment 437), neither of these causes was in such active operation, and hence the actual amount of CO_2 present in the vessel was relatively less, causing a partial removal of the oxygen previously conferred.

SECTION XIX.—DEPOSITED CARBON THE SUPPOSED PARTIAL CAUSE OF CERTAIN APPARENT ANOMALIES IN THE COMPOSITION OF BLAST FURNACE GASES.

The subject of carbon deposition has been considered at some length, which, it seems to me, is deserved, *i.e.*, if the supposition be correct that to this operation we are probably indebted for the expulsion of the last portions of oxygen from the ore.

The fact has been often observed that after a certain depth in the furnace is reached, the quantity of oxygen in the ascending gases, compared with the nitrogen, goes on increasing, proving that it is due to some other source than the blast. The extent of this increase will be most fitly gone into when the general composition of furnace gases comes up for consideration.

The source of the additional oxygen to the gaseous contents of a furnace as we descend, has formed the subject of enquiry to Ebelmen and others, but no answer, I believe, has been accepted as satisfactorily explaining all the phenomena of this apparent anomaly of the smelting process. Dr. Percy dismisses all the conclusions arrived at as untenable, and gives it as his opinion that speculation will be vain without the aid of further experimental evidence. This author truly enough observes that everything "points to carbonic oxide as the great agent of reduction in the blast furnace," and then proceeds to say that "oxide of iron is readily and completely reduced by the action of this gas even at a red heat." My impression is that the whole error lies here, oxide of iron, I conceive, never is, and, I suspect, most probably never can be *completely* reduced by carbonic oxide—on the contrary, this gas, in its purest state, slightly oxidizes iron already reduced, and from the oxygen so communicated, the metal is probably never wholly freed until it arrives at a state of fusion when carbon, most probably that derived from the dissociation of CO, aided possibly by other substances, effects that perfect reduction hitherto considered as being within the power of carbonic oxide to accomplish. The subject is one of much interest from a scientific as well as from a practical

point of view, and can be appropriately resumed when analyses of gases are given with the intention of gathering from them the nature of the change going on in the furnace itself. The information obtained from smelting Cleveland stone will be contrasted with that afforded by furnaces working different materials, in the hope of eliciting some general expression applicable to all.

I do not intend to have it inferred that all the increase of oxygen found in the gases as we approach the tuyeres, and due to other sources than the blast, is derived from the dissociation of carbonic oxide. There is found in almost all pig iron more or less silicon, and the difficulty of separating this substance from the oxygen with which it is combined in the minerals supplied to the blast furnace is so well known as to render it impossible to conceive that silicon can be resolved into its constituents under less powerful action than that to be found alone in the focus of most intense temperature. The presence, therefore, of silicon and, if we believe some analyses, of calcium and the metallic bases of other earths will account in part for the excess of oxygen in question. To what extent oxidation, due to carbon impregnation, may be retained by the iron as it descends through the furnace can only be inferred from those analyses of the gases, which, in the first instance, drew attention to the increasing disproportion of oxygen and nitrogen as we approach the lower region of the furnace.

One thing, I imagine, is certain, viz., that the quantity of carbon which is deposited from carbonic oxide in the furnace is extremely large. The experiments, already described in these pages, have shown that in a few hours iron may become impregnated with many times its weight of carbon when exposed to the action of heated carbonic oxide. The bursting action of carbon as it is deposited in the substance of ores of iron has also been alluded to; and I have, upon a previous occasion,* described the breaking up of blocks of ironstone into a coarse powder by accumulations of carbon. This occurred on exposing pieces of Cleveland calcined ore to the escaping gases of a blast furnace, having a temperature varying from 280 to 450°C. (536 to 842°F.).

Since then, circumstances necessitated the breaking of a considerable aperture in the side of a furnace 50 feet from the summit. There, pieces of coke and lime were found mixed with a large quantity of

* "Transactions of Iron and Steel Institute," Oct., 1869.

a powdery substance, consisting of partially reduced ore and blac carbonaceous matter, but no pieces of ironstone were visible. Th same thing must have been observed by most practical smelters in the hearth of a furnace upon removing a portion of its contents for repairs, &c. Fragments of the fuel and flux are taken out so little changed as to be immediately recognised, but a piece of partially reduced, or fused ironstone large enough to be identified is of rare occurrence, its place, apparently, being taken by a large bulk of coarse dark looking powder.

Recently at the Clarence Works two furnaces have been blown out. Upon such occasions there are always found in the sides hollow spaces produced by extraordinary local wear. These frequently have a capacity of several cubic feet; and, generally speaking, the cavities in question in the lower parts of the furnace are closely packed with portions of the materials under treatment. These consist invariably of a black disintegrated mass containing pieces of coke and lime, but the ironstone appears to have entirely disappeared and to have been converted into the powdered substance just described.

SECTION XX.—OFFICE PERFORMED BY DEPOSITED CARBON.

The excess of oxygen in the furnace gases near the tuyeres, when compared to the nitrogen they contain, led to the belief first, I believe, enunciated by Ebelmen that this oxygen was derived from the minerals at the moment they passed into the fused state prior to falling into the well of the furnace, the deoxidation being completed by the fuel. This explanation always appeared to me unsatisfactory. The coke, so far as the eye can determine, in that portion of the furnace, is in pieces of a certain size, certainly not in that condition of intimate contact to insure deoxidation when the melted mixture of iron and slag is pouring down at the rate of a ton every ten minutes. The amount of oxygen in excess over the nitrogen is often equal to a considerable quantity of Fe O for every ton of iron produced, and that this should run down like water among fragments of coke and only leave ·25 per cent. of Fe in the slag, looking at the affinity between Fe O and silica, seems incredible.

The difficulty of want of requisite contact between carbon and metal retaining still a portion of oxygen is removed by the theory of a plentiful deposition of C. The deposited carbon also in all probability is the source of C in the pig iron.

Exp. 440. To judge of the properties of the deposited carbon in both these respects, a portion of factitious Fe_2O_3 which had been exposed to CO, and found to consist of

Fe	... ...	85·26
C	... ...	8·00
O	... ...	6·74
		—— 100

was placed in a crucible with a double lid, and the whole enveloped in fireclay and well dried for 18 hours in an air bath.

Fifteen grammes (containing 12·77 Fe) was exposed to a forge fire for 18 minutes, at the end of which time a button was obtained, weighing 11·65 grammes. A portion of it was digested in Cu SO_4 and the residue burnt in O. In this way the button was found to consist of

Fe	... ...	99·0
C	... ...	1·0
		— 100

It did not appear, however, that oxide of iron, with minutely divided carbon in its pores, was more easily reduced or carburized than when the iron oxide was mixed with finely powdered charcoal.

Exp. 441. F_2O_3 obtained by the same process as that used in the previous experiment. It was reduced to such an extent that 100 Fe was associated with 9·04 O. A mixture of this substance and charcoal was made to resemble as near as possible the composition in Exp. 440, viz.:

Fe	... ...	85·89
Charcoal	... ...	8·07
O	... ...	6·04
		—— 100

15·73 grammes (containing 13·51 Fe) was heated for 15 minutes in the same fire as in the previous exp. A button weighing 13·44 grammes was the result. The C was estimated as before. The button contained 1·65 per cent. of C, and consisted of—

Fe	... ...	13·22	= 98·4
C	... ...	·22	= 1·6
		——13·44	= —— 100

In exp. 440, there is less oxygen to remove, which may account for the more perfect reduction of the Fe and increase in carbon contained in the button.

In both cases there is a disappearance of C, not accounted for by the loss of O, and probably due to a small and different quantity of air obtaining access to the contents of the two crucibles. Speaking generally, the two experiments justify the inference that the deposited carbon is highly efficient in reducing Fe_2O_3, the more so that this substance is introduced in a state of very fine division.

SECTION XXI.—GENERATION AND BEHAVIOUR OF CO_2 IN THE BLAST FURNACE.

The amount of heat evolved by the combustion of carbon into carbonic oxide and carbonic acid has been variously stated by different experimenters. The discrepancy, however, among the most recent investigations is inconsiderable, and, therefore, whatever figures are adopted, it is unlikely the calculations based thereon will be far from being correct. The numbers actually made use of in this work are 2,400 units for carbon burnt to CO and 8,000 when burnt into CO_2.

As a mere matter of heat development, it is obviously a subject of great importance to have in the blast furnace the fuel so burnt as to form as large a proportion as possible of CO_2, inasmuch as the heat evolved from this is 3·33 times that produced by the formation of CO.

As illustrative of this let us suppose two furnaces, from one of which (A) the carbon is given off in the gases so as to generate 20 vols. CO_2 for every 100 vols. of CO, and in the other (B) 40 vols. of CO_2 per 100 vols. CO.

Equal volumes of CO and CO_2 contain the same weight of carbon; hence the heat development is for—

A,	100 pts. carbon	burnt to CO,	$100 \times 2{,}400 = 240{,}000$	ht. units.
	20 do.	do. CO_2	$20 \times 8{,}000 = 160{,}000$	do.
	120 do.	do. thus, ...	400,000	do.

Or, $\frac{400{,}000}{120} = 3{,}333$ heat units, per one part of carbon.

While it is for—

B,	100 pts.	carbon	burnt to CO	$100 \times 2{,}400 = 240{,}000$	ht. units.
	40	do.	do. CO_2	$40 \times 8{,}000 = 320{,}000$	do.
	140	do.	do. thus, ...	560,000	do.

Or $\frac{560{,}000}{140} = 4{,}000$ heat units, per one part of carbon.

Hence the increased amount of heat got in the second case is 20 per cent. more than that obtained in the first case.

Practically we may consider all the carbon burnt in the hearth to commence its ascent in the furnace as CO. The CO_2, which finds its way into the gases, owes its origin to the expulsion of that contained in the limestone, to the deoxidation of the ore and to carbon deposition by the reaction already so fully described.

It by no means however follows that carbonic acid produced by any of these means escapes as such from the blast furnace. Where CO_2 is generated in the furnace by the reduction of the ore, and is itself subsequently reduced to the state of CO, the evolution and absorption of heat balance each other. On the other hand it generally happens with the CO_2 introduced in combination with other substances, that the CO produced causes a heat absorption of 5,600 units for each unit of carbon without any set off whatever.

Let us consider the behaviour of the carbonic acid contributed by the limestone used in the manufacture of pig iron, for this is the usual vehicle by means of which CO_2 finds its way in its combined form into the blast furnace.

It is a well known fact that, provided the temperature is high enough, CO_2 is rapidly converted into CO by carbon ($CO_2 + C = 2\ CO$). The subject for consideration, therefore, is the temperature at which lime parts with its CO_2, and that at which the CO_2 parts with one equivalent of its oxygen.

All authorities agree that calcium carbonate commences to lose its carbonic acid at a low red heat, but does not part with all under a much higher temperature.

Exp. 442.—It is certain that Ca O retains the last portion of its CO_2 with some tenacity, for I found that in an hour or thereabouts, at a red heat, quick-lime absorbed CO_2 in such quantity that it consisted of 84 of Ca O and 16 of CO_2, equal to ·242 equivalent of CO_2 to one of lime.

Exp. 443.—Nine hours' exposure under similar circumstances to

those of the previous experiment gave a substance consisting of 81 Ca O and 19 CO_2, or one equivalent of the base to ·298 of the acid.

Exp. 444. 2·129 grammes of coke, previously ignited for two hours in a covered crucible to expel hydro-carbons, &c., was mixed with 1·310 grammes of marble in coarse powder. The mixture was placed in a combustion tube, and a stream of nitrogen, purified by pyrogallate, passed over it to sweep out any volatile matter given off. A dull red heat was maintained for 40 minutes, and the gas passed through a potash bulb.

The mixture lost ... 0·085 = to 6·5 per cent. of the weight of the [marble.
Potash bulb gained ·073 = „ 5·6 „ CO_2

$C + CO_2$ reduced to CO ... 0·9

Exp. 445. The above experiment was repeated on 1·710 grms. of coke, and 1·394 grms. of marble.

The mixture lost ... 0·200 = to 14·3 per cent. of the marble.
Potash bulb gained ·132 = „ 9·4 „ „

$C + CO_2$ reduced to CO ... 4·9

Hence the carbon taken up by CO_2 to form CO was—

$4·9 \times \frac{12}{56} = 1·1$ per cent.

And hence the CO_2 lost = 13·2 „

In this case the experiments lasted only 20 minutes, but the temperature was higher in the previous trial. The marble lost about two-sevenths of its CO_2, but of it at this temperature only one-third of the CO_2 liberated was converted into CO.

These two experiments go to prove that where there is nothing to restrain the emission of CO_2 from the Ca CO_3 this gas is given off at lower temperatures than that required for its conversion into CO by C, and in experiment 445, out of 13·2 parts of carbonic acid expelled only 4·9 less 1·1 or 3·8 (about one fourth) was resolved into CO.

These, however, are not the conditions under which limestone is exposed in the blast furnace. The nitrogen there is accompanied with large quantities of CO, and some CO_2, and as the latter substance has a strong tendency to unite with lime, particularly at temperatures of moderate intensity, it follows that its presence

must constitute a barrier to the free exit of that contained in the mineral. Indeed, so strong a barrier is this, that calcium carbonate, it is asserted, has been fused under pressure without parting with its CO_2.

To establish a condition of things more analogous to that obtaining in the blast furnace, the following experiments were tried.

Exp. 446. Hard blast furnace coke and limestone were pulverized to the size of mustard seed, and dried at 250°C. (482°F). These were placed in weighed boats in distinct portions in a combustion tube, separated and retained in their positions by plugs of asbestos. A current of CO_2, dried by SO_4H_2, was conducted through the tube for one hour to sweep out all the air. Heat was then applied so as barely to melt zinc—perhaps, 410°C. (770°F.)—and the current of CO_2 continued for one hour. The issuing gas was passed through potash, and was entirely absorbed, except about 30 ccs. These were found to be composed of 47 per cent. of CO, estimated by explosion, and 53 per cent. N due from air in apparatus, or contained in the liquid HCl used for generating the CO_2. The limestone had lost ·33 per cent. of its weight, but this must have been due to moisture, for it contained before the experiment 42·7 per cent. of CO_2; and after it, 42·8 per cent. A second trial gave a portion of unabsorbed gas which contained 68 per cent. of its volume of CO.

These two experiments show that at melting zinc in an atmosphere of CO_2 limestone loses none of its acid, but that CO_2 itself suffers a trifling amount of decomposition from the action of the coke.

Exp. 447. A similar trial was made at a heat just perceptibly red in daylight, which was continued for the same time—1½ hours. In this case about 70 ccs of unabsorbed gas were collected, which was composed of CO 79·3 and N, &c., 20·7. The loss of weight suffered by the limestone was ·58 per cent., but none of this was CO_2. On the other hand, the quantity of CO_2 decomposed is something like four times that which was effected in experiment 446.

Measures were now adopted to ascertain, if possible, the action of coke, on the large scale, on the carbonic acid as it exists in the blast furnace. For this purpose, that at Wear was selected using Cleveland roasted ore and limestone also previously calcined. The capacity of this furnace is 17,500 cubic feet.

Exp. 448.—Two observations, taken over a period of half an hour, gave the composition of the gases by volume, as follows:—

CO_2 11·6 ... CO, 28·1 ... H, 1·8 ... N 58·5=100

A charge of materials was now put on, consisting of—

Coke	... ...	26 cwt.
Calcined limestone		11 „
do.	ironstone	56 „

The composition of the gases, taken at the end of one hour after this, was—

CO_2 ... 13·1 ... CO, 22·7 H, 2·7 ... N, 61·5=100

So that the action of the minerals introduced had been to increase the proportion of CO_2, and this, it is assumed, would be due to the action of the Fe_2O_3 on CO.

Fifty-two cwts. of coke were now put on without any ore or calcined limestone, in the expectation that the CO_2 would be reduced in quantity by the coke ($CO_2+C=2$ CO), and no additional CO_2 generated, owing to the absence of any increase in the quantity of Fe_2O_3.

About seven minutes after the coke was introduced, the gases were found to consist of—

CO_2 11·1 ... CO 25·2 ... H, 1·3 ... N, 62·4 = 100

In three quarters of an hour afterwards, they contained—

CO_2 12·7 ... CO 23·5 H, 2·0 ... N, 61·8 = 100

At this composition they continued for something like two hours, no fresh materials being introduced.

From these facts, it is inferred, that of the coke, there is a portion, at least, which acts at comparatively low temperatures in reducing CO_2 to CO; what that portion is, will be considered when the question of fuel is examined. The temperature of the escaping gases was not taken, but previous examinations enable me to state that at the time of putting in the 52 cwts. of coke, they would stand at about 500°C. (932°F.)*

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* It must be remarked that it is not an easy matter to obtain results from such an experiment as No. 448, from which well-defined conclusions can be drawn, owing to the fluctuations in the composition of the gases, which constantly take place. Four analyses in Exp. 448 have been selected from a dozen, as illustrating an action, which actual trials in the laboratory had proved to happen when coke is exposed to the action of CO_2 at moderate temperatures.

Tabulated, the whole of the actual figures were as follows:—

CO_2 11·6 ... CO, 28·1 ... H, 1·8 ... N, 58.5 = 100 (given above.)

From this, and previous experiments, it may be inferred that as carbonic acid, in an atmosphere of CO_2, is only sparingly given off at a full red heat, and CO_2 commences to suffer decomposition at 400° to 500°C. (752° to 932°F.), all the CO_2, entering the furnace combined with Ca O, leaves it as CO.

This view of what really takes place in the furnaces of the Cleveland district is further confirmed by the CO_2 in the gases never exceeding that due to the reduction of Fe_2O_3, and to the dissociation of that portion of CO, which furnishes the carbon found in the pig iron.

Supposing, however, that heated carbon were unable to reduce the CO_2 of the limestone to CO, long before all this acid is expelled from the flux, there must be a large quantity of metallic iron present, or iron containing so small an amount of oxygen that it will act very energetically on CO_2, at such temperatures as that at which, by far the greater portion of the limestone suffers decomposition. In support of this, experiments 70 to 80 are referred to, in which Fe was proved to split up CO_2 with great ease, the metal being oxidized at the expense of the carbonic acid.

In this section, no account is taken of the small quantity of CO_2 which may result from the action of the blast upon the fuel in the hearth of the furnace, nor of the minor quantities to be met with occasionally in its higher regions, probably, alternately generated by CO and a suboxide of iron, or carbon deposition, and decomposed by the action of heated carbon, or heated spongy iron: for, however numerous may be these changes, the result is about equivalent to a final escape (in the case of larger furnaces of the Cleveland district) of CO_2, corresponding to Fe_2O_3 reduced, and the C found in the pig iron produced.

Put on coke, limestone, and ironstone:
Three analyses during next hour, gave of CO_2—
10·7 per cent.; 11·7 per cent.; 19·1 per cent. = mean 13·8 of CO_2.
At end of 30 min. CO_2 13·1 ... CO, 22·7 ... H, 2·7 ... N, 61·5 = 100 (given above.)
Put on 52 cwt. of coke: in 15 minutes from beginning to charge this, and immediately after its introduction was finished (average 7½ minutes), analysis gave—
CO_2, 11·1 ... CO, 25·2 ... H, 1·3 ... N, 62·4 = 100.
A second analysis, 17 minutes after, gave 4·3 per cent. CO_2—
Soon afterwards there was found—
CO_2, 12·7 ... CO, 23·5 ... H, 2·0 ... N, 61·8 = 100 (given above.)
Five analyses during the ensuing two hours, afforded—
CO_2, 11·9—22·7—12·0—15·8—11·8 = mean 14·8 per cent. of CO_2.

SECTION XXII.—ON HYDROGEN; ITS SOURCE, AND POSSIBLE INFLUENCE IN THE BLAST FURNACE.

The carbonic oxide, by means of which those changes described in the previous pages are effected, has been, excepting in a few cases, this gas either in its pure state or mixed with carbonic acid. Where these two gases are generated by the action of atmospheric air upon carbon, there is, of course, a large quantity of nitrogen present; but there exists no reason, that I am aware of, for asserting that so far as the action of these two compounds of oxygen and carbon are concerned nitrogen behaves otherwise than somewhat blunting their power by mere dilution.

Whether carbonic oxide and carbon, without any addition whatever, would be capable of bringing about the results actually obtained in the blast furnace, is a subject which, so far as absolute experience is concerned, will probably for ever remain a subject of speculation.

In the actual process of smelting iron, the foreign gaseous substances which are found accompanying the carbonic oxide and its associated nitrogen, are in comparatively small quantities. Among them hydrogen, and one or two compounds which this element forms with carbon, are invariably present. Hydrogen itself, doubtless, owes its origin to the moisture contained in the atmosphere, which varies considerably in its amount.

The power of atmospheric air to contain water is, as is well known, greatly affected by temperature. With the thermometer at 10°C. (50°F.) the proportion of volume of aqueous vapour existing in any gas with the barometer at 30 ins., is ·01333; whereas, at 20°C. (68°F.) it is ·02406,* or nearly twice what it is at the former temperature. The occasions, moreover, are rare when the atmosphere is completely charged with that quantity of water it is capable of holding with any given state of the barometer and thermometer. M. Kämtz, at Halle, found as a mean of several years' observation, the following to be the relative humidity for

* Faraday—Manipulations.

each month—*i.e.*, the existing percentage of the quantity required for complete saturation :—

Jan.	Feb.	Mar.	Apl.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.
85·0	79·9	76·4	71·4	69·1	69·7	66·5	61·0	72·8	78·9	85·3	86·2

Taking a cubic mêtre of air at 10°C. (50°F.), and 760 *mm.* barometer, to weigh 1·25 kilogrammes, and to contain, as it will do, 9·39 grammes of water as saturation, we have the amount of moisture present equal to 0·75 per cent.

The smallest quantity of air forced by the blowing engine into one of the furnaces smelting Cleveland ore, will be a trifle above five tons for each ton of pig iron produced. Calling it 100 cwts., we might thus have 0·75 cwt. of moisture entering the tuyeres per ton of metal made, provided the atmosphere were saturated with aqueous vapour. According to M. Kämtz's observations, the average extent of saturation is 75 per cent. over the whole year. So that with the barometer at about 30 ins. (29·92), and the thermometer at 10°C. (50°F.), we have to deal with 0·56 cwts. of water per ton of iron.

The instant this water meets with the highly heated carbon and iron in the hearth of the furnace, it is, of course, resolved into hydrogen, the fuel or metal taking up its oxygen, and therefore, we shall have present, near the tuyeres, for each ton of metal, one-ninth of the above quantity of free hydrogen, or 0·062 cwts.

Taking the calories of burning hydrogen to water to be 34,000, the above weight of this gas, obtained by the decomposition of atmospheric moisture, represents an absorption of 2,108 calories or, heat units. It will be, hereafter, shown, that coke, burnt with hot blast to the state of oxidation it is found in the waste gases of the larger description of furnace, gives out about 3,700 heat units, so that the splitting up of the water conveyed into the hearth of such a furnace as that we are dealing with, requires the heat afforded by 0·57 cwts. of coke. This fact will account for some of those minor changes in the working of a blast furnace, which are well known to all observant smelters; for, supposing, at one time the atmosphere to contain only one half the aqueous vapour it is capable of holding, and then suddenly to become wholly saturated; in the former case, the heat of 0·38 cwts. of coke would suffice for setting free the

hydrogen, whereas, in the instance of entire saturation, 0·77 cwts. of coke would be needed, or a difference of nearly half a cwt.

This view, of the effect of the presence of aqueous vapour, explains, also, the injurious results of allowing water from the tuyeres to be admitted into the hearth of an iron furnace.

If we take the case of a production of two tons of metal per hour, which is an ordinary make in a Cleveland iron furnace, something like ten tons of blast will be required in this time. Let it be imagined, that, during this hour, a leaky tuyere suffers 9 cwts. of water to flow in among the materials filling the crucible—which is only 1·68 gallons per minute:—

The heat absorbed will be 1 cwt. of H at 34,000	=	34,000 heat units.
Less that evolved from 8 cwt. O transformed into CO; this will combine with 6 cwt. of carbon, evolving 6 × 2,400 calories ...	=	14,400 „
Leaving a balance representing loss of		19,600 „

and, taking 3,700 units, as before, to represent the heat from each cwt. of coke, we have 19,600 ÷ 3,700, being 5·4 cwts. of coke for two tons of iron, or upwards of 2½ cwt. for each ton, resulting from the admission of about 1¼ gallons of water per minute.

In the case of water, there is a further loss of 640 calories for each cwt., for its conversion into vapour, which is equivalent to 9 cwt. H_2O × 640, or 5,760 cwt. heat units. This, upon the ton of metal will represent about 0·78 cwts. of fuel, making in all a loss of 3·5 cwts. from this apparently trifling cause.

Whether this decomposition of H_2O is a source of real loss heat over the entire furnace, will depend on the circumstance of its condition at the moment of its exit from the throat, *i.e.*, if the evolved H is reconverted into H_2O by the iron ore, the heat absorption and production will exactly balance each other. Notwithstanding this, there is always a serious derangement in the working of the smelting process by the admission of H_2O, due to the fact that heat is absorbed where it is most wanted, and evolved when its presence is a questionable benefit. An endeavour will be made to ascertain the condition of the H thus generated as it leaves the furnace, but unfortunately, the estimation of the exact quantity present in the gases is a subject attended with certain difficulties, and the numbers

obtained are liable to further disturbance by the introduction of hydrogen compounds from another source.

The method of analysis adopted was necessarily a very rough one, as the time that would have been occupied by more refined methods prevented their adoption in cases, where, perhaps, a dozen different determinations had to be made simultaneously; for this reason, too, the verification of the eudiometers employed was neglected, as also the errors introduced by slight changes of temperature and pressure of barometer during the analysis.

The examinations were conducted in eudiometers, as supplied commercially, where irregularities in the graduation, which may falsify the results obtained, are usually observable; and moreover it was impossible to read off the volume contained within less than ·05 cc.; so that, irrespective of additional errors from fluctuations of temperature of the laboratory atmosphere, the minimum discrepancy in reading off 10 ccs. of gas would be *plus* or *minus* 0·05 cc., or 0·5 per cent. This departure from truth is subject to increase from other causes, which might easily double the possible error.

In the analyses given in these pages, the plan adopted was to introduce about 10· ccs. of gas into the eudiometer, and read off the volume. Oxygen was then added and the volume noted, after which the mixture was exploded by electricity, and the contraction noted after cooling, and, finally, the CO_2 was absorbed by KHO. In some instances the gas used had its original CO_2 absorbed, in others not, and in such cases the CO_2 formed by explosion was got by subtracting the CO_2 present as such (found by a separate trial) from the total CO_2 after explosion.

The CO_2 produced by the explosion, together with that originally contained in the gas, averaged usually about 3·5 ccs., hence the error of 0·5 per cent. would be 1·5 per cent. on the carburized gases present, and it might easily, from the other causes spoken of be double this; in which case, an error of 6 or 7 per cent. on its amount might easily be introduced in the estimation of the contraction, which was not much more than half the volume of the CO contained.

Assuming, which is unproved, that the gases contained only CO, CO_2, H, and N, the hydrogen was calculated from the excess of contraction over half the CO; hence, as there was a possibility of 6 or 7 per cent. of error in the fundamental datum from which the hydrogen is calculated, and as this gas rarely exceeded 7·5 per cent.

of the vol. of the CO, there is room for attributing the whole quantity to experimental error. It is true that such errors would probably in the end balance each other; but still the amount of H, given as that contained in the gases, cannot be regarded as strictly correct, under the most favourable supposition.

Beyond the source of error just described it is probable, indeed certain, that more or less CH_4, and possibly other hydro-carbons, &c., are always present to some extent. The CO_2 produced, therefore, would not be wholly due to CO, nor would the contraction be wholly due to CO+H, and this throws additional error on the hydrogen determination.

To avoid the sources of error attendant upon the eudiometric mode of analysis, a quantity of the furnace gas was collected in a mercurial aspirator, and subjected to examination in the following way:—

Exp. 449. A quantity of Cu O was placed in a tube and heated red hot, and over it three litres of gas from the top of the Wear furnace were conducted, previously being passed through KHO, SO_4H_2, and $Ca Cl_2$ tubes, so that all CO_2 moisture, &c., were removed. In this way, all the H and CO existing in the furnace gas were converted into H_2O and CO_2, and being collected in the usual method were weighed, and the ratio of H to CO thus obtained.

In two trials made with the same sample of gas, the following were the results:—

(A) gave 1·711 of CO_2 and 0·096 H_2O
(B) „ 1·177 „ CO_2 „ ·070 H_2O

Hence the ratio of H to 100 of CO in the gases is—

	By weight.	By volume.
In the case of (A) ...	0·98	13·7
do (B) ...	1·04	14·5
Mean ...	1·01	14·1

An analysis of the same sample of gas, performed with the help of the eudiometer, the composition was ascertained to be—

CO_2	9·25	
CO	28·25	
H	1·30	
N	61·20	
	———	100 volumes,

in which the ratio of H to CO, by volume, is only 4·6 to 100, instead of 13·7 and 14·5 to 100.

Exp. 450. A second sample was taken, two days after that used in the previous experiment, and it gave the following results—Two weight determinations were made, as formerly—

A gave 0·86 of H per 100 of CO: and B, 0·84 mean 0·85
A = vol. 12·04 „ H „ CO: „ B, 11·76 do. 11·90

Analysed in the ordinary way, this sample not only gave no H, estimated by contraction, but there was a *minus* quantity, amounting to 1 per cent. of the whole, the figures being—

CO_2	+	8·0	=	8·0
CO	+	27·7	=	27·7
H	—	1·0	=	nil.
N	+	63·3	=	62·3
		100·0		100·0

Exp. 451. A sample was next drawn from an orifice, 6½ feet above the tuyeres. An analysis was made of the gas, in the state in which it issued from the furnace, and after it was freed from CO_2, previously to being passed over the Cu O. Their composition was as follows:—

	No. 1. Furnace Gas.	No 2. Same Furnace Gas, freed from CO_2
CO_2	1·5	0·0
CO	34·2	35·0
H	1·3	1·1
N	63·0	63·9
	100·0	100·0
In these cases, ratio of CO to N,	54·3 to 100	54·7 to 100

Passed over the heated Cu O, No. 2 gave by weight—

A, ·63 of H pr. 100 of CO; and B, 0·54 of H pr. 100 vol. CO mean 0·58

Or, estimated by volume,—

A, = 8·82 vol. of H per 100 vol. CO; B, 7·56 vol. H per 100 CO mean 8·19.

whereas, the ratios, by the two eudiometer trials given above, were 3·8 and 3·11 vols. of H per 100 of CO, respectively.

It is possible that the results afforded by the method pursued in the three experiments just described may be influenced to a slight extent by moisture present, but every precaution was taken to avoid this by aspirating warm air through the apparatus, while the Cu O was red-hot, and by the use of several Ca Cl_2 tubes.

The weight of gases produced by 100 to 103 cwt. of blast may be taken at something like 135 cwt., containing, as has been already shown, 0·062 cwt. of hydrogen, derived from atmospheric moisture, which corresponds with 0·046 per cent. of the entire weight of the escaping gases.

An ordinary quantity of CO leaving the furnace such as that at Wear is 35 cwt. per ton of iron; hence the H per ton is—

From the top 100 : 1·01 :: 35 : ·35 cwts. of H.

At 6½ feet above the tuyeres the CO for a similar quantity of metal will be about 46 cwt.

Hence 100 : ·58 :: 46 : ·26 cwts. of H.

As might be expected the gases from the top charged as they are with any hydro-carbon existing in the coke, are somewhat richer in H than the sample taken lower down, and where the fuel must have parted with all its volatile constituents.

If the figures given in the above experiments are correct, we must assume either that upon the occasions when they were made, the atmosphere was unusually moist (saturated with moisture at a much higher temperature than that assumed in the calculations of hydrogen introduced in the blast (10°C.=50°F.), or that considerable leakage took place at the tuyeres, or that the hydrogen evolved from the coke employed (existing there as hydro-carbons), considerably exceeded that due to the moisture in the blast.

These experiments, and those of other chemists certainly warrant the belief that H may exist to the extent of from 5 to 10 per cent. of the entire volume of CO found in the escaping gases, *i.e.*, when coked coal, or charcoal is the fuel. Upon this supposition, certain experiments were undertaken with a view to ascertain whether the presence of this amount of H might not sensibly affect the action of reduction; for, it had been observed in some of the eudiometric trials, made for the purpose of acquiring a knowledge of the amount of CO present that explosion, when the necessary O was added, was often attended with some difficulty. To overcome this, a small quantity of H was added, and then the combustion was rendered easy, although the united volume of the two inflammable gases in some cases did not exceed that of CO alone in other mixtures, which exploded with difficulty.

Magnus mentions the lowest temperature at which H can reduce Fe_2O_3 to be 315° to 371°C. (600° to 700°F.)

Exp. 452. Five grammes of calcined Cleveland ore were placed in a tube, to which heat could be applied by an oil bath. For half an hour purified and dry hydrogen was passed over it at a temperature of 104° to 127°C. (220° to 260°F.) The ore at the end of this time, on titration by permanganate, showed no sign of reduction.

Exp. 453. The same quantity of ore, from the same specimen, was similarly treated, the temperature, however, being 199° to 227°C. (390° to 440°F.) In this case there was apparently a small amount of reduction.

From this experiment it would appear as if Cleveland ore began to yield its oxygen to CO (*vide* experiment 17), and to H about the same temperature.

As happens with CO, hydrogen appears to be able to abstract the first portions of oxygen very rapidly, and at a very low heat, but perfect reduction is only accomplished after the lapse of some time, and assisted by a considerable elevation of temperature.

Exp. 454. About 250 grains of Cleveland ore were placed in a porcelain tube, and pure H dried in the usual way was passed over it for four hours at a good red heat—maximum of single Hofmann's furnace. At the end of this time the ore still retained a portion of its oxygen, known by what was in the ore, and comparing it with the H_2O formed which had ceased for some time before the expiry of the four hours. The tube was then removed to a coke fire raised to a white heat, when H_2O immediately reappeared, and in about one hour the proper weight due to the quantity of O in the ore was collected in the $Ca\,Cl_2$ tube.

To determine the relative action of H and CO on Cleveland calcined ore, a mixture of 12 volumes or thereabouts of the former to 100 of the latter was made and introduced into a Pepys' gasholder

Exp. 455. On leaving their receptacle, the mixed gases passed through three bulbs and two U tubes containing pyrogallic acid and KHO, (in order to retain any oxygen accidently present); bulbs with solution of potash; two tubes, containing pumice saturated with SO_4H_2; and finally through a $Ca\,Cl_2$ tube. The mixture thus purified and dried was led over 63·65 grains of heated ore placed in a platinum boat, introduced into a glass tube, behind which there were a $Ca\,Cl_2$ tube, potash bulbs and tube containing solid potash, to intercept any H_2O or CO_2 which might escape from these bulbs.

Before applying heat all air was expelled by passing 3 litres through the apparatus and the purity of the gas tested. It consisted of, by analysis—

CO	... ...	88·2
H	... ...	10·6
N	... ...	1·2
		—— 100

The tube containing the ore was heated for 1½ hour to such a point that a piece of zinc was kept melted, but the temperature was never visibly red. A current of gas was maintained until the apparatus was cold.

The ore, on being heated in oxygen, furnished 4·40 grains of CO_2 equal to 1·20 of deposited carbon, which corresponds to 4·61 per 100 of metallic iron present.

The total H_2O collected was	0·95 gr.	= 0·85 Oxygen.	
Do. CO_2 do.	22·75		
From which deduct that due from reaction of $2\,CO=C+CO_2$	4·40		
	18·35	= 6·67	„
Together		7·52	„
The ore weighed less than at beginning	6·25		
To which add C represented by 4·4 CO_2	1·20		
Together		7·45	„

The close agreement between the two amounts of oxygen lost, is a proof of the trustworthiness of the experiment.

In this case, something like 68 per cent. of the original oxygen was removed in a period of 1½ hours, and 4·6 parts of deposited carbon obtained per 100 of Fe present.

On referring to experiments 25 and 26, it will be observed the amount of deoxidation exceeds that obtained by pure CO, and, speaking generally, the carbon impregnation is also greater.

Exp. 456. The previous experiment was repeated at maximum temperature of Hofmann's furnace—very bright red heat—for one hour, weight of ore used 68·85 grains, heated in porcelain tube.

The ore, on combustion in oxygen, gave 1·4 grains CO_2 equal to ·38 of carbon = about 1·36 per 100 of Fe present.

Total H_2O collected was	0·65 grains	=	0·58 oxygen.
„ CO_2 do.	22·95		
From which deduct CO_2 from reaction of $2CO = C + CO_2$	1·40		
	21·55 „	=	7·84 „
			8·42 „
Ore weighed less than at beginning	7·90		
To which add C represented by 1·4 CO_2	·38		
			8·28

which again is a close approximation.

The percentage of original oxygen expelled was about 70.

Exp. 457. 61·8 grains of same ore was next exposed to the maximum (white) heat of a coke furnace for 40 minutes, and gas from the same sample as the two previous experiments passed over with similar precautions. For 25 minutes the action was so energetic that the gas was all converted into CO_2, for almost the whole was absorbed by the solution of potash. Afterwards, this absorption ceased almost entirely, and on removing the residue from the tube, it was found completely fritted and appeared perfectly metallic—the altered structure no doubt having interfered with the process of reduction.

The ore, on now being heated in oxygen, gave 0·30 CO_2 equal to ·08 C or ·32 per cent. estimated on metallic iron present.

Total H_2O collected was	1·60 gr.	=	1·42 Oxygen.
Do. CO_2 do.	14·15		
From which deduct CO_2 from reaction $2CO = C \times CO_2$	·30		
	13·85	=	5·04 „
Together			6·46
Ore weighed less than at beginning ...	6·55		
To which add C represented by 0·30 CO_2	·08		6·63 „

Loss of original oxygen about 60 per cent.

Contrasting the three experiments we have the following ratios calculated on 100 parts of the ore used:—

Temperature ...	Melting zinc ...	Bright red ...	White heat.
Loss of O per hour	7·8	12·	15·9
Carbon deposited	1·27	·55	·19

The ratio of volumes was 12 of H to 100 of CO, while the reducing action of H to CO was as follows:—

Temperature.	Melting zinc.	Bright red.	White heat.
Ratio of H to CO	12·8 to 100	7·4 to 100	26·2 to 100
Weight for weight—reducing action of H is more energetic than CO	14·9 times.	8·6 times.	30·5 times.
The action of H and CO are—			
Loss of O per hour with H	·89	·83	3·5
Do. CO	6·91	11·17	12·4
Together...	7·80	12·00	15·9

Thus the action of CO increases with the temperature, while that of H was the same at a red heat as at melting zinc, but was four times as great at a white heat; and, as regards the latter temperature, it is likely the action of H and CO would have given higher results had the operation not been suspended by the partial fusion of the ore. These conclusions, however, are subject to this error; part of the water produced in these experiments may have come from the action of hydrogen, not on the ore, but on the CO, or the CO_2 produced by the action of CO on the ore. This will be referred to hereafter.

Notwithstanding the apparent superiority, as evinced by the previous experiments, of the energy of H to reduce an oxide of iron, when compared with CO, it must be recollected that the method, by means of which, the comparison has been made, by no means represents the conditions of the blast furnace. There, these two gases, during their ascent among the materials, are constantly meeting, not only metallic iron, and this metal in all states of reduction, but also large quantities of carbon, both in a more or less heated state.

Actual observation, at the blast furnace itself, inclines me to the belief that whatever change, hydrogen, once set free near the tuyeres may experience during its progress to the throat, it finally leaves the furnace, for the most part, unchanged.

The temperature of the materials, at the charging apparatus,

is such, that, as a rule, the escaping gas never inflames, and any small quantity which escapes, does so without undergoing combustion; the moment, however, a tuyere commences to leak, the gas takes fire, just as a small quantity of H in the eudiometric researches produced explosion in a mixture not previously influenced by the electric spark.

The appearance of flame, just referred to, is often the first intimation of a leaking tuyere, and is announced by the workman 80 feet above the seat of the evil. It is obvious, that, did the hydrogen liberated in the manner described pass to the state of steam by deoxidizing iron oxide, the presence of aqueous vapour would retard, instead of promoting combustion of the gas with which it was mixed.

This view of the behaviour of H seems also in some measure confirmed by the experiments and calculations already referred to.

Notwithstanding the view of the action of H in the blast furnace, just expressed, viz., that it escapes without being converted into water, its presence, once formed, may, possibly, not be a matter of indifference.

We have already seen, that to restrain the oxidizing influence of CO_2, a certain quantity of CO is necessary. There seems no reason to doubt, why, to some extent at all events, H may not replace this CO, although the H itself may never be changed.

It is also possible that the presence of H may influence the various actions going on in the interior of the furnace, so that although there may be no actual gain, so far as a mere evolution of heat is concerned, by the resulting H not passing again to the state of HO_2, the effect of this influence may be to facilitate some of the chemical changes which accompany the smelting of iron.

With the intention of discovering whether a mixture resembling somewhat in composition that of blast furnace gases had its reducing energy heightened by the presence of H—

Exp. 458. A mixture was prepared, which, on analysis, was found to consist of—

CO_2	... ...	14
CO	... ...	30·5
O	... ...	·3
N	... ...	55·2
		100

in which the CO_2 to CO is as 46 to 100 volumes.

Calcined Cleveland ore was exposed to this at a temperature of melting zinc, in the lead bath, for 15 hours, without the oxide of iron losing any oxygen.

In another case (experiment 95), calcined Cleveland ore, exposed to a mixture of 100 vols. CO and 50 vols. CO_2, at a temperature of melting zinc, in 5½ hours lost ·9 out of its 42·8 of O, which is equivalent to 2·09 per cent. of the original quantity.

Exp. 459. An experiment was tried, but in this case the temperature reached a higher maximum, for antimony had melted. The composition of the gas was—

CO_2	... ...	15·9
CO	... ...	33·5
O	... ...	·4
H	... ...	4·2
N	... ...	46·0
		—— 100

In this the CO_2 is to CO as 47·3 volumes to 100, or the volumes of CO and H jointly are as 100 to 42 of CO_2.

In this experiment, in 10½ hours, the loss of oxygen amounted to 11·7 per cent. of that originally in the ore.

In experiment 106, the proportion of CO_2 to CO was as 31 to 100, and therefore more energetic in a reducing point of view. Nevertheless, in 10½ hours, at a temperature of melting zinc, the quantity of O removed was only 2·9 per 100 Fe, or 6·8 per cent. of the original oxygen.

In experiment 102, at a low red heat, calcined Cleveland ore was stated to lose 5·8 of oxygen out of the 42·8 found in Fe_2O_3 equal to 13·55 per cent. The time of exposure was 6 hours, and the gas contained 50 of Co to 100 of CO.

Exp. 460. Applying the mixture used in experiment 459, also to Cleveland calcined ore in a tube, at a low red heat, for 6½ hours, 38 per cent. of the original oxygen was expelled without any carbon, however, being deposited.

Where the loss of O was the greatest, it must be mentioned, the proportion of CO_2 was occasionally somewhat less than in the case with which it is compared; besides, a perfect similarity of temperature might not obtain; on the whole, however, there seems to prevail through all the experiments just described a distinctly

marked tendency of H to facilitate the reduction of oxide of iron by CO.

This may not proceed so much, if at all, from the superior affinity possessed by H over CO for oxygen, but from the action exercised by H over nascent CO_2. It has been demonstrated how materially the reducing influence of CO is affected by the presence of CO_2; hence, if by any means the quantity of CO_2 can be again resolved into CO, not only is the CO_2 lessened thereby in amount, but nascent CO is liberated, which probably is more energetic in its action on an oxide of iron, than the same gas applied in the ordinary way.

The following experiments illustrate not only that H decomposes nascent CO_2 at very low temperatures, but also that its presence facilitates the escape of this acid from Ca CO_3, which of itself may have a certain importance in the actual working of a blast furnace.

To obtain nascent CO_2 recourse was had to Ca CO_3, to which heat was applied and a current of different gases passed over, without which this substance, as is well known, does not part readily with its acid.

	Substance used.	Gas passed over.	Temptre.	Time. Min.	CO lost by Ca CO_3	CO_2 absorbed by K HO.	CO_2 reduced.	H_2O formed.
Exp. 461.	Limest...	Air	Dull red	30	3·4	3·5	0	0
,, 462.	Do. ...	Air	Bright red	40	13·5	13·6	0	0
,, 463.	Do. ...	CO_2	Low red	90	Nil	0	0	0
,, 464.	Do. ...	CO_2	Bright red	30	10·7	0	0	0
,, 465.	Do. ...	CO_2	do.	90	10·86	0	0	0
,, 466.	Marble...	H.	Melt. Zn.	40	1·03	0·19	0·84	0·55
,, 467.	Limest...	H	Dull red	30	3·21	·38	2·83	1·07
,, 468.	Do. ...	H.	Bright red	30	40·56	21·42	19·14	7·44
,, 469.	Marble...	H.	do.	20	43·47	23·47	20·00	8·67

The above are estimated on 100 parts of the substances employed.

The limestone contained 43·61 per cent. of CO_2. The marble was pure white Carrara; hence = 44·0 per cent. CO_2. The water found did not correspond precisely with the theoretical quantity corresponding to CO_2 reduced to CO, as will be perceived from the following statement:—

In experiments	466. *a*.	467. *b*.	468. *c*.	469. *d*.
H_2O found	·55	1·07	7·44	8·67
Theoretical $H_2O = CO_2$ reduced to CO	·34	1·16	7·83	8·18

It has been pointed out by Wanklyn (Watt's Dictionary, Article Marsh Gas), that the action of H on marble gives rise to more H_2O, than that corresponding to the reduction of CO_2 to CO. Experiments *a* and *d* confirm this; the different result got in *b* and *c* probably arises from the expulsion of combined water in the *limestone* used in these experiments.

In the blast furnace itself the heated carbon may produce the same effect as the hydrogen, *i.e.*, the CO_2 set free from the flux may be resolved into CO. To ascertain whether hydrogen also accelerated the decomposition of CO_2 in the presence of carbon, coke from which volatile matters had been expelled by two hours' exposure to a high temperature was mixed with carbonate of lime.

Expts.	Substance mixed with coke.	Gas passed over.	Temptre.	Time. Min.	CO_2 lost by $CaCO_4$.	CO_2 absorbed by KHO.	Total CO evolved.	CO_2 reduced to CO.	H_2O formd.
470.	Marble...	N.	Dull red	40	6·5	5·6	0·9	...	
471.	Do.	,,	Full red	20	14·3	9·4	4·9	...	
472.	Limest.	H.	Melt. Zn.	45	3·42	·53	...	2·89	1·2
473.	Do.	,,	Bright red	40	42·6	14·00	18·6	...	

Thus, here again, the action of H in decomposing the nascent CO_2 is quite perceptible.

SECTION XXIII.—ON AMMONIA IN THE BLAST FURNACE.

The action of free ammonia, in all probability, will not be very different from that exerted by pure hydrogen, looking at the feeble affinity which exists between its component parts. The behaviour of this alkali, when brought in contact with heated oxide of iron would warrant this belief, for it appeared to remove O as freely as hydrogen did.

Exp. 474. A current of NH_3 passed over calcined Cleveland stone, removed 2·85 per cent. of the original oxygen in twelve minutes, the temperature being short of redness.

Exp. 475. The above experiment was repeated at a low red heat, when the loss of weight of the ore corresponded to 17·71 per cent. of the original oxygen.

The alkaline base of these salts may be derived from more sources than one. It may possibly, but perhaps not very likely, be

the result of the union of atmospheric nitrogen with the nascent hydrogen produced by the decomposition of aqueous vapour. It may be due to traces of nitrogenous matter not thoroughly expelled from the coal in the process of coking, or it may be generated by the decomposition of some cyanogen compounds which are formed in the lower part of the furnace.

Exp. 476. In a series of experiments, particulars of which will be given later on, the gases from the Wear furnace were passed through water. In the saline substance so condensed, NH_4 was found to an extent corresponding to per cubic metre, as follows :—

	Above tuyeres, about 8 ft.	24½ ft.	60ft.	76½ ft.	Top.
Grammes ...	3·47 ...	2·38 ...	2·94 ...	2·50 ...	4·92

Taking the weight of the escaping gas, as before, to be 135 cwts. per ton of iron, which represents about 4,500 cubic metres of gas, measured at 0°C. to 760° mm. pressure, we may have 22·14 kilogrammes of NH_4 for the quantity of metal, which is only equal to 4·92 kilogrammes of hydrogen: the NH_4, in all probability, existing at first as cyanide of ammonium, NH_4CN.

It is, moreover, possible that a portion of the NH_4 may be due to a decomposition of the alkaline cyanide contained in the fume of the gases themselves in the act of collection, but whether this be true, or not, it is obvious, from the foregoing statement, that ammonia, from its very small quantity, may be altogether omitted from the reducing agents of the furnace.

Before quitting the subject of ammonia, it may be mentioned that on one occasion, a couple of years ago, when trying the effect of using uncalcined Cleveland ironstone in the furnace, the escaping gases were cooled down to such an extent as to permit copious condensation of aqueous vapour in the gas tubes. This water, dropping from the pipes, formed stalactitic, crystallized masses, which, on analysis, were found to consist of—

Insoluble (probably Fe_2O_3)	1·0
Chloride of ammonium	52·9
do. iron	14·7
do. zinc	6·6
do. sodium	tr.
do. calcium	tr.
Water	24·8
	100·

SECTION XXIV.—ON HYDRO-CARBONS IN THE BLAST FURNACE.

The observations just made, with regard to hydrogen will, most likely hold good with the hydro-carbons, which, in minute quantities, may be emitted from the coke. The hydrogen they contain, probably, will behave in a similar way to that described when speaking of the action of this element, either in its pure form, or when associated with N in N H_4 salts. The carbon, too, in the shape of hydro-carbon, will also, in all likelihood, act pretty much as carbon deposited from CO.

If we have, however, to judge of the behaviour of hydrogen, when it exists in larger quantities, by the analysis given by M.M. Bunsen and Playfair, in their examination of the gases of a furnace fed with raw coal, this substance would appear to be absorbed in some way between its emission and its ascent through the materials in the furnace.

The following table contains a statement, by weight, of the composition of the furnace gases at Alfreton, examined by these chemists, and calculated from their volumetric figures:—*

Below top, distance of	5 ft.	8 ft.	14 ft.	20 ft.	24 ft.	34 ft.
Nitrogen	57·40	56·75	56·09	60·88	57·41	59·87
Carb. acid	12·60	16·06	15·74	16·92	15·77	·00
do. oxide	26.90	20·95	21·20	19·33	25·08	38·60
Light Carb. Hyd.	2·20	4·86	4·17	2·55	1·32	·00
Hydrogen	·50	·48	·97	·34	·40	·24
Olefiant gas	·40	·90	1·72	·00	·00	·00
Cyanogen					tr.	1·20
	100·00	100·00	99·89	100·02	99·98	99·91
These figures give of pure H	1·11	1·82	2·26	0·98	·73	·24
Or, H per 100 of N	1·93	3·21	4·03	1·61	1·27	·40

In these figures, the H present is much larger at the points 8 ft., and 14 ft. below the throat, than at that five feet below the same point. This diminution, as the gases ascend, if the analysis represents an average composition, may be due to the action of H or its

* "Transactions of British Association for the Advancement of Science, 1845."

compounds with carbon, on the ferric oxide; or it may be due to the prevalence of that action H is capable of exercising on CO_2, already described.

Between the level of 8 and 5 feet below the top the proportion of CO_2 ought to increase, instead of which it has materially fallen off in quantity; thus, at the former point 100 of N is accompanied by 28·3 CO_2, whereas at the latter the proportion of carbonic acid has fallen to 21·9 per 100 of N. It is further to be observed that the CO is largely increased in quantity in the case when the CO_2 has fallen off. At the 5 feet level 57·4 N is associated with 12·60 CO_2 and 26·90 CO,

together, equal to 14·93 of carbon.

At the 8 feet level 56·75 nitrogen carries with it—

16·06 CO_2 and 20·95 CO, equal to 13·36 C,

the first of these proportions being at the rate of 26·01 of C per 100 of N, and the second in the proportion of 23·54 of C per 100 of N. Thus, it would appear, that there has been an abstraction of oxygen from the CO_2, which might have been effected by the H.

The idea that the presence of so large a quantity of hydrogen and hydrogen-compounds may account for the apparent inconsistencies in the analyses of M.M. Bunsen and Playfair is based on the supposition that their figures represent an average composition of the gases given off at the different heights of the Alfreton furnace. That the analyses themselves were correct, admits of little doubt, looking at the skill of the experimenters and the evident pains bestowed upon the labour. I cannot, however, gather from the elaborate description of the work that more than one specimen of gas was subject to examination. Now, in the case of a furnace using coke, the composition of the gases is subject to great fluctuation, and this must prevail to a much larger extent with one using raw coal, which will emit a larger or lesser quantity of hydro-carbons, according as the period of collection may be hastened or delayed after the charge of fuel has been introduced. This observation of source of error is of course particularly applicable to the gases collected near the top of the furnace. Again, the mode of collection by permitting an iron tube to descend with the charges, and drawing the gases through it, is open to a serious objection. The tube itself, when 26 feet of it was suspended in the furnace, would, in the greater portion of its length, be very highly heated, in which state

it would be sure to alter the composition of the gases, either by CO_2 being resolved into CO by the oxidation of the iron of the tube, or by the action $2\ CO = C + CO_2$ produced by the same cause. The synthetical proofs given by M.M. Bunsen and Playfair of the correctness of their analyses are likewise, in my judgment, open to objection; for they are founded on the assumption that all the fixed carbon of the coal is burnt to CO at the tuyeres, and that the CO_2 of the limestone escapes as such. It is more than doubtful whether the CO_2, entering any furnace in combination with Ca O, leaves it without being reduced to CO, and this change is produced directly or indirectly by carbon. To what extent this carbon, in the case of the Alfreton furnace, is furnished by the coke of the coal, and to what extent by the hydro-carbons, I am not in a position to say. Again, a notable quantity of the CO_2 generated by the action of CO on the $Fe_2\ O_3$ by the reduction of the latter in such a small furnace would not leave it as such, but would also be reduced to CO. The fact of this being the case, and the reason, will be hereafter explained.

The power of hydrogen to seize oxygen from a combination of this element and carbon is not confined to that constituting CO_2, for it appears that CO is capable of being split up by its means.

Exp. 477. Hydrogen was obtained from sulphuric acid and zinc, passed through KHO, and through two bottles of sulphuric acid to dry it.

Carbonic oxide was procured from ferro-cyanide of potassium, purified by means of two bottles of KHO, one bottle of $Ag\ No_3$, and dried by sulphuric acid.

The two gases, maintained in about equal quantities, were united by a T shaped tube, dried by $Ca\ Cl_2$, and conducted through a porcelain tube filled for 12 inches with pumice-stone, which latter had been previously ignited for 20 minutes without losing weight, To expel air, the mixed gases were passed through the apparatus for two hours. Heat was then applied and maintained for one hour, zinc melting freely on the top of the tube, its lower side being at a dull red heat. During this time a current of the CO and H was led over the heated pumice and then through a tube filled with $Ca\ Cl_2$ to potash bulbs, behind which was another tube filled with $Ca\ Cl_2$, to intercept any moisture carried off from the alkaline solution.

At the end of the hour there was an increase of weight due to H_2O of 1·2 grains and of CO_2 0·1 grain.

Exp. 478. Observing the same precautions as those just described, a current of the mixed gases was passed over the pumice stone at a full red heat. In 1·33 hours the operation had to be suspended, owing to the potash bulb stem getting choked with K_2CO_3. The chloride of calcium tube gained 4·6 grains, and the potash bulbs 1·2 grains.

The pumice stone was now withdrawn and found to be blackened; it was heated in oxygen and the resulting gas passed over red hot Cu O. It afforded CO_2 equal to ·43 grains of carbon.

The sum of these two experiments is—

Water formed	1·2 + 4·6 = 5·8 grs.	= 5·2 grs. oxygen.
CO_2 collected	·1 + 1·2 = 1·3	„
C do.	·43	„

Exp. 479. A third trial was made in which a stream of CO without H was passed, with similar precautions, as in the previous experiments, over heated pumice for two hours at a full red heat.

The chloride of calcium gained ... ... ·3 grains.
Potash bulb gained... ... ... ·6 „

The pumice suffered no change in appearance, no carbon being deposited.

SECTION XXV.—ON THE PRESENCE OF THE METALLIC BASES OF THE FIXED ALKALIES IN THE GASES OF THE BLAST FURNACE.

The presence of the fixed alkalies in a blast furnace is not difficult to account for. Both fuel and ore frequently, if not invariably, contain traces of potash, and it may be of soda; at all events, the quantity of water required to cool the coke employed in smelting iron will, in most cases, contain common salt, and thus furnish the second-named substance.

The brilliancy of the flame of burning furnace gas, spoken of by M. Tunner, and known to all smelters, is suggestive of sodium being formed in the lower parts of the furnace, where the atmosphere is clearly of a highly reducing character, for in colour and general

appearance the combustion greatly resembles that of the gas emitted during the manufacture of this metal. Messrs. Bunsen and Playfair, in their celebrated paper on the gases from iron furnaces,* mention collecting a substance, about 3 feet above the tuyeres, at the Alfreton furnace, which, evolving hydrogen on the addition of water, they considered to contain potassium or its compound with carbonic oxide.

The gases at most blast furnaces have to pass a distance of many yards before they arrive at the fire-places, where they are applied for producing steam or heating the blast. At the Clarence Works, the flame under one of the boilers, situate about 100 yards from the nearest furnace, was examined, in company with Mr. Norman Lockyer, F.R.S. On application of the spectroscope, the sodium lines were very distinct, but there was no sign of those of potassium. In the heating stove fire-places, within 50 yards of the top of the furnace, the sodium lines alone were also visible.

In one of the cinder runners, the liquid slag had made for itself a kind of rough tube through which it flowed. Out of an aperture near the furnace gaseous matter issued, as often happens, and at a few feet further from the furnace, was a similar orifice. At both, a flame, several inches in length was burning. On viewing the flame nearest the furnace through the spectroscope, the potassium lines were distinctly visible accompanying the sodium lines, but at the more distant flame the latter were alone perceived. The total disappearance of the potassium lines in so small a space is remarkable. Upon another occasion, Dr. Wright observed the lithium line (α in Bunsen's Chart), in a residue left on evaporating a solution of a saline matter, collected by aspirating gas from the Wear furnace, at a point six feet above the hearth. Compared with the potassium lines, the line of lithium was faint, but still distinctly perceptible.

Exp. 480. In the hope of detecting either potassium or sodium in the gases of the Wear furnace, a hole was drilled in the side 6 feet above the tuyeres for the purpose of withdrawing the gaseous contents of the furnace.

By analysis, the gas at two points near this aperture was shown to have the following composition upon two different days.

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* "Report British Association for Advancement of Science, 1845."

	Hole 11 above tuyere. Hole 6 feet above tuyere.			
	Exp. 481. First Day.	Exp. 482. Second Day.	Exp. 483. First Day.	Exp. 484. Second Day.
CO_2	Nil.	0·3	Nil.	Nil.
CO	35·6	35·3	35·4	33·1
H	1·3	1·0	0·2	1·3
N	63·1	63·4	64·4	65·6
	100·	100·	100·	100·

Thus the region at and around the orifice in question was unmistakably of a highly reducing order.

Into the orifice was introduced an iron pipe with an elbow, so that its outer end could be dipped into mercury, upon the surface of which floated a layer of petroleum to prevent the oxidation of any alkaline metal. The bend of the pipe was provided with a screw plug, to clear away any obstruction in case of need.

A rapid current of gas was kept up for three hours, at the end of which time the bottle, which had risen in temperature to near 100°C. (212°F.), contained a large quantity of sublimed alkaline salts.

In no case was there any evolution of H on putting the clean mercury, resulting from these experiments, into water, or on addition of H Cl; nor did it swell up by addition of NH_4Cl.

Exp. 485. The issuing gas from a hole nearly midway between the two (8 feet above tuyere) was similarly received in mercury, during four hours, and near which the gases contained a mere trace of CO_2. (*Vide* experiments 481 to 484.) The mercury so treated exhibited no evidence of the presence of K or Na.

Exp. 486. A comparative experiment was made by dissolving 0·1 gramme of clean Na in 650 grammes of mercury; the resulting amalgam gave a slight effervescence with H_2O; a stronger one with H Cl; and slightly swelled up with NH_4Cl.

This experiment, then, points to the conclusion that neither K nor Na, in the metallic state, was present upon the occasion alluded to.

SECTION XXVI.—ON THE PRESENCE OF ALKALINE CYANIDES IN THE BLAST FURNACE.

As might be expected, a substance rich in carbon, as cyanogen is, with its constituents held together by feeble affinity, is a powerful reducing agent.

Exp. 487. One vol. of Cy, even when mixed with two vols. CO_2 at a temperature short of redness, deprived a specimen of calcined Cleveland stone of 3·42 per cent. of its oxygen in fifteen minutes. In about the same time, when the heat was enough to soften the glass tube, one-fourth of the O was expelled.

In all probability, however, free cyanogen does not enter into the composition of furnace gases; it will be shown hereafter that the results got by Messrs. Bunsen and Playfair are susceptible of another explanation that does not involve the existence of free cyanogen. Potassium cyanide, however, is well known as a powerful reducing agent; its *modus operandi* depending, however, not on the production of CO_2, but on the direct combination with oxygen to form cyanate KCNO.

M. M. Bunsen and Playfair estimated that in every cubic metre of gas at a point 2·75 feet above the level of the tuyere, at the Alfreton furnace, there was to be found 2·6 grammes of cyanide of potassium, estimated by drawing 380·8 c. ins. through water during 24 minutes. Besides this quantity, they estimated that three or four times as much was condensed in the pipes of their apparatus, making in all 8 to 10 grammes per cubic metre.

This furnace was 40½ feet high, and 11 feet diameter at the widest part. That at Wear is 80 feet high, by 20½ feet at the widest diameter, containing about 17,500 cubic feet, and at it the following trials were made.

The apparatus employed at the last named furnace to ascertain the total weight of soluble salts contained in its gases, consisted of a short elbow pipe, inserted in the wall of the furnace, about 8 feet above the tuyeres. The perpendicular leg of the pipe was immersed 3 inches in water, contained in a large stoneware carboy, from which proceeded another pipe in connection with a gasholder about 30 inches in diameter. The rising of this

gasholder indicated the volume of gas which had passed through the water. At the end of the operation the elbow pipe was withdrawn and washed with water; and the solution thus obtained was added to that contained in the carboy, the total bulk being then measured and analyzed.

The mode of analysis was as follows:—A known fraction of the total liquid (after uniform mixture and filtration) was boiled for a few minutes with KOH and Fe SO_4 solution; by this means the whole of the cyanide present became converted into ferrocyanide; SO_4H_2 and Fe_2Cl_6 were now added to the liquid, until an acid reaction was obtained; Prussian blue was thus precipitated, which, after some hours standing, was collected on a filter, washed, decomposed by pure KOH, and finally titrated by permanganate after addition of pure SO_4H_2; it was found impossible to get agreeing results by any other method, as the finely divided metallic iron, or partially reduced Fe_2O_3 mechanically blown in along with the fume, always converted more or less of the cyanide into ferrocyanide in the first instance.

A second fraction of filtered liquid was evaporated to dryness, and weighed after desiccation at 120°C.; the total constituents soluble in water were thus obtained, consisting essentially of cyanide, ferrocyanide, and carbonate of potassium, sodium, and a little ammonium, and traces of lithium; lime and zinc were present in small quantity, with traces of sulphate. The alkali metals were determined by treating the residue after evaporation to dryness with SO_4H_2, whereby a mixture of sulphates of K, Na, Fe, &c., was produced; the mixed sulphates of K and Na were separated by precipitation with NH_3 and NH_4 oxalate, evaporation to dryness and ignition; and the per centage of SO_3 determined in the mixture; from these two data the K and Na were calculated by the ordinary process for indirect analysis.

The "other substances" referred to in the results about to be quoted consequently consist mainly of Fe united with the alkali metals and Cy as ferrocyanide; O and CO_2, similarly united as carbonates; and water of crystallization not expelled at 120°C.; along with the traces of lithium, zinc, calcium, SO_3, &c. The collection of the gas extended over about three-quarters of an hour, and the volume of gas which passed into the holder averaged about 200 litres (⅕ cubic mêtre).

The following were the results obtained in the manner described, calculated in grammes in one cubic mêtre of the gases. Measured at 0° C and 760 *m.m.* pressure.

		Above tuyeres.				Exit pipe after leaving furnace.
		Ex. 488.	Ex. 489.	Ex. 490.	Ex. 491.	Ex. 492.
From hearth		8 feet.	24 feet.	60ft.	76ft.	
K	Grammes	73·47	14·15	9·18	16·05	3·47
Na	,,	39·23	17·84	16·69	7·99	1·72
Cy	,,	49·06	15·76	7·67	5·94	4·73
Other substances	,,	61·31	15·10	9·85	19·38	11·40
Total constituents soluble in water		223·07	62·85	43·39	49·36	21·32

This experiment was repeated at the aperture 8 feet from the tuyere, on the waste gases upon eleven different occasions, upon what the following weights in grammes were calculated to be carried off in every cubic mêtre.

8 feet from tuyeres.	Ex. 493.	Ex. 494.	Ex. 495.	Ex. 496.	Ex. 497.	Ex. 498.	Average
Date, 1870. July	14th.	15th.	19th.	22nd.	26th.	28th.	
K	42·83	26·56	28·90	18·34	26·60	5·13	24·73
Na	3·86	3·61	4·25	2·75	5·05	6·75	4·38
Cy	19·00	12·93	17·32	11·34	20·61	9·16	15·06
Other substances	31·01	39·03	27·53	14·91	22·69	20·78	25·99
Total	96·70	82·13	78·00	47·34	74·95	41·82	70·16

Gases as they leave furnace. July		Ex. 499. 15th.	Ex. 500. 19th.	Ex. 501. 22nd.	Ex. 502. 26th.	Ex. 503. 28th.	Average
K	Grammes	9·44	12·01	7·74	4·50	1·52	7·04
Na	,,	1·76	3·29	·94	1·39	2·77	2·03
Cy	,,	4·00	6·60	3·57	2·91	1·79	3·77
Other substances	,,	20·52	23·81	10·05	7·92	8·70	14·20
Total		35·72	45·71	22·30	16·72	14·78	27·04

It must be mentioned that the experiments noted as having been performed the same day were not done absolutely simultaneously, but immediately after one another, the whole process for both lasting perhaps a couple of hours.

A source of error in the observations made at the lower orifice, is the following:—Portions of fused alkaline salts (cyanides, &c.), or of coke impregnated with them, may have been mechanically carried over into the water by the current of gas, thereby increasing the apparent amount of these substances, per cubic mêtre of gas. The amount of cyanogen, however, is probably, in all cases, understated, inasmuch as alkaline cyanides are readily decomposed by

by carbonic acid: hence, it is probable that hydro-cyanic acid vapour was carried away by the gases, after passing through the water, owing to the presence of CO_2 in the gases, the error from this cause being greater at the highest orifices, where the percentage of CO_2 is the largest; in these cases, too, the first error does not appreciably obtain, as the temperature is insufficient to flux the alkaline salts, and, moreover, the pressure of blast is considerably reduced, thereby rendering the mechanical carriage of coke, &c., less probable.

At the hole 8 feet from the tuyere we have the Cy varying from 9·16 grammes per mêtre to 49 grammes, the Ka from 5·13 to 73·47, and the Na from 3·6 to 39·23.

In the gases, as they leave the furnace, at a temperature below that of melting zinc, we have the following gradations—

K	from	1·52	to	12·01	grmms. per c. metre.	
Na	„	0·94	„	3·29	„	„
Cy	„	1·79	„	6·60	„	„

There is no doubt that the actual quantity of saline matters existing in a fused state in the lower part of our blast furnaces, is really very considerable, for, on driving an iron bar into the contents, it always came out coated with these substances. Remembering how small a quantity is introduced in the raw materials employed for each ton of metal, the only way to account for the accumulation of cyanides, &c., is by supposing that, as the alkaline salts are volatilized, they are in great part condensed by the cool substances entering the furnace, and so brought back to the vicinity of the tuyeres. Without pretending to say to what extent this cumulative action goes on, it is clear it is in operation, for, as a rule, the higher up in the furnace the samples of gas were collected, the less alkaline matter is there found associated with its contents.

In the analyses just quoted, the Cy is not present in sufficient quantity to form K Cy + Na Cy with the whole of the alkali metals present.

If the results, obtained in the experiments just described, were entirely to be depended on, we may infer that, as the vapour of cyanide, *e.g.*, of potassium, ascends through the furnace, it absorbs oxygen, probably from the residual O in the partially reduced Fe_2O_3, thereby producing cyanate, KCNO; this substance is known to be decomposed at a high temperature, the products of its decom-

position, however, have not been studied; potassium vapour, CO and N are in all probability produced, or, perhaps, oxide of potassium, carbon, and nitrogen. The potassium compound produced, be it what it may, is carried upwards by the ascending gases till it becomes more or less condensed and filtered out by the cooler materials in the upper part of the furnace, which thus become highly impregnated with alkalies.

On arriving again in the region where the temperature is intense enough to enable K or Na to determine the union of atmospheric nitrogen with carbon, fresh cyanide is generated, and the whole process gone through again; probably, the reason why a limit exists to the length to which this cumulative process can be carried, is—that when it reaches a certain point, the alkalies are carried off in the slag and fume, through non-sufficient filtration of the gases from the solid alkaline compounds.*

Sometimes the cyanides formed would appear to be almost entirely decomposed, inasmuch as considerable quantities of alkaline salts have been upon one or two occasions collected at the Clarence Works containing scarcely a trace of Cy.

In their report on the Alfreton furnaces, Messrs. Playfair & Bunsen represent free cyanogen as one of the constituents of furnace gases, a little way above the hearth. The results obtained by these gentlemen, however, are perfectly compatible with the supposition that their collecting tubes become lined with fairly divided alkaline cyanides, and that the slow passage along the tube of slightly moist gas containing carbonic acid, caused the evolution of hydrocyanic acid vapour; it does not appear to be proved that N and C can directly combine to form C_2N_2, although in presence

* The following is an analysis of slag produced at the Clarence furnaces, smelting Cleveland ironstone:—

SiO_2	27·65
Al_2O_3	24·69
CaO	40·00
MgO	3·55
FeO	·72
MnO	·35
S	1·95
K_2O	·46
Na_2O	·99
P, possibly as P_2O_5	·26
	100·62

of (nascent ?) K or Na, KCN is readily formed under suitable conditions.

It seems almost hopeless ever to realise a true estimate of the actual quantity of cyanides present at one time in a blast furnace. We have first the everchanging proportions in which these and their associated salts exist in the vaporous state in the furnace gases, and there is, moreover, an unknown quantity, almost impossible to estimate correctly, of saline matter impregnating the solid contents of the furnace.

To arrive at any satisfactory conclusion with respect to the end, if any, served by the presence of these carbon-nitrogen compounds, by direct experiment, is attended with equal difficulty from the fact of it being almost impossible to imitate on a small scale the agencies at work in the blast furnace.

It is open to enquiry whether even carbon in its solid form, when accompanied by so large a quantity of CO as exists in the blast furnace, can *wholly* reduce an oxide of iron, and that, in consequence, the presence of cyanogen salts, which are never entirely absent, may not be an indispensable ingredient in the smelting process. It is possible that where these are absent, minute quantities of oxide of iron carried into the metal itself may, perhaps, constitute the difference between the conditions requisite for producing grey and white iron. No doubt it will be alleged that the last-named quality of metal is made with less fuel and presumably at a lower temperature than grey iron, but both descriptions are produced at a temperature sufficient to reduce oxide of iron, and carburize the metal. This temperature suffices to afford, chemically speaking, two substances which may be so identical in composition as to be considered one and the same; the trace of oxygen, I am supposing present, having hitherto eluded detection.

There is, I apprehend, much to learn yet in this somewhat intricate question, and I regret the few experiments in this direction have not done much to extend my knowledge on the subject,

Exp. 504. A mixture of Fe, Fe oxide, and C being the residue of lead bath experiments contained ·65 per cent. of its weight of C. None of the Fe was soluble in iodine.

One gramme was placed in a combustion tube, and had a current of CO passed over it for 35 minutes, at a temperature gradually rising to melting zinc. Out of 31·6 Fe, 16·17 was soluble in iodine.

Exp. 505. One gramme of the above was mixed with its weight of K Cy, and similarly treated to previous experiment. Out of 31·6 Fe, 25·9 was soluble in iodine.

Exp. 506. One gramme pure Fe_2O_3 was placed in a porcelain tube, and exposed for one hour to a rapid current of CO. At the end of this time it was washed by decantation, and dissolved in H Cl. In the case of Fe_2O_3, the washing was also performed, so as to render the treatment in all respects comparable with that adopted in the next experiment. Titrated with permanganate, 5·3 per cent. remained as Fe_2O_3.

Exp. 507. Another gramme of the same Fe_2O_3 was mixed with its own weight of Liebig's K Cy, containing 70 per cent. of Ka Cy. After exposure to CO, and treatment in all respects similar to previous experiment, 3·8 per cent existed as Fe_2O_3.

Exp. 508. 500 grains hæmatite containing 66·6 per cent. Fe
2,000 „ Liebig's K Cy
1,000 „ Pounded glass
Perfectly fused into a very dark glass, and in it was a globule of white iron the size of a hemp seed.

Exp. 509. Pure Fe_2O_3 prepared by calcining Fe SO_4, reduced until it contained only one-tenth its original O—
500 grains taken
1,000 „ Liebig's K Cy
1,000 „ Pounded glass
No button obtained, but small globules, which gave off H on the addition of H Cl. Black vitreous mass.

Exp. 510. 500 grains Fe_2O_3, same as previous experiment.
100 „ Charcoal powder
1,000 „ Liebig's K Cy
1,000 „ Pounded glass
Fused into a light coloured glass, in which was a well-formed button of white iron.

Exp. 511. 500 grains of pure Fe_2O_3
100 „ Charcoal powder
1,000 „ Pounded glass
Fused as before, but without any K Cy; glass dark colour, containing a well-formed button of grey iron.

In all these experiments the heat was gradually applied so as to afford time for deoxidation.

There is one proof of a practical kind which might lead one to infer that K Cy is not an indispensable agent in the operation of iron smelting. None of the materials used contain beyond a mere trace of K_2O or Na_2O. It is clear, therefore, in putting a furnace into blast, some time must elapse before the cumulative process, already alluded to, can have produced any marked effect on the quantity of these alkalies in the lower part of the furnace. If, therefore, their presence is absolutely necessary for proper reduction or carburization, one would naturally expect that the furnace would have to work sometime before these alkaline cyanides had accumulated in sufficient quantity for effecting the supposed end. True, it is that the first "cast" of a new furnace is often white, but, in a regular way, with proper precautions as to temperature of blast, &c., in a very short time foundry iron is produced. The accepted explanation of running white iron at first is the coldness of the hearth which, of course speedily disappears after 12 to 24 hours blowing.

The following statements are taken from the Clarence charging books, and exhibit the period at which grey takes the place of white iron immediately after laying on the blast.

Blowing in No. 3 furnace, containing 6,000 cubic feet.

Filled furnace with—

Coke, 55·7 tons; calcd. ironstone, 28·3 tons; burnt lime, 10·85 tons.

Laid on blast—

Charged coke, 34·1 tons; calcd. ironstone, 45·0 tons; burnt lime, 12·15 tons.

Tapped, 2 tons No. 2, and 7 tons No 3 grey iron.

Blowing in No. 2 furnace, containing 11,500 cubic feet.

Filled furnace with—

Coke, 115·4 tons; calcd. ironstone 91·6 tons; limestone, 34·1 tons.

Laid on blast—

Charged coke, 35·9 tons; calcd. ironstone, 58·8 tons; limestone, 16·8 tons.

Tapped 15½ tons No. 3 grey iron; and in three days, this furnace was making No. 1.

Blowing in No. 1 furnace, containing 11,500 cubic feet.

Filled furnace with—

Coke, 119·0 tons; calcd. ironstone, 99·3 tons; limestone, 35·9 tons.

Laid on blast—

Charged coke, 36·75 tons; calcd. ironstone, 60·50 tons; limestone, 17·40 tons.

Tapped, 4 tons No. 2; 5 tons No. 3.

Blowing in No. 8 furnace, containing 15,500 cubic feet.

Filled furnace with—

Coke, 146·9 tons; calcd. ironstone, 143·2 tons; limestone, 16·4 tons.

Laid on blast—

Charged coke, 34·4 tons; calcd. ironstone, 54 tons; limestone, 16·4 tons.

Tapped, 9 tons mottled.

On third day iron was ... ... No. 4
„ fifth „ ... ... „ 3
„ eleventh „ ... ... „ 1

Blowing in No. 5 furnace, containing 25,400 cubic feet.

Filled furnace with—

Coke, 215·9 tons; calcd. ironstone, 231·8 tons; limestone, 74·15 tons.

Laid on blast—

Charged coke, 36·1 tons; calcd. ironstone, 63·9; limestone, 17·8 tons.

Tapped, 16 tons white iron, first cast.
2 tons No. 3, and 14 tons No. 4, second cast.
On sixth day, furnace made No. 1 iron.

Taking the most favourable case for illustrating the present argument, viz., that of No. 3 furnace, the iron run the first cast was No. 2 and No. 3. Now, all this would be made out of a portion of the materials required to fill the furnace, which would be in the proportions of about 43 tons of coke,
22 „ calcined ironstone,
8·5 „ raw limestone.

The usual amount of ash contained in the coke being used was about six per cent., so that the total quantity of coke burnt, 43 tons, would give 2·58 tons of ash. I am not aware that potash ever exceeds two per cent. of the weight of the ash, so that the 2·58 tons of ash could not amount to above ·051 tons or about one cwt. According to experiments 493 to 498, the average quantity of Na associated with K is about one-sixth, so that we have

K_2O 1 cwt., contains K = to Cy ·54 cwt.
Na_2O 0·16 do. Na = Cy ·13

Total cyanogen ·67

of itself far too small a quantity, one would think, to influence the manufacture of nine tons of iron. This calculation, however, assumes all the alkali in the minerals is converted into cyanides of their basis, that none finds its way into the slag, and that the whole of that which is volatilized in the lower part of the furnace is condensed and serves again in the reduction—a supposition as we have seen opposed to direct observation. If half the above quantity or ·33 cwts. were really acted on by the iron in process of reduction it would amount to about four lbs. of Cy per ton of iron.

It may be urged, and with justice, that for the first few tons of iron made, the quantity of coke per ton of metal being immensely in excess of that ordinarily consumed, the cases of it, and a furnace in regular working order, are far from being parallel ones. This is, no doubt, the fact, but we are at present dealing with the hypothetical supposition that, as CO has been proved not to be able completely to reduce iron oxide, some other agent is required, and that this agent may be an alkaline cyanide. The only other probable agent is carbon, probably in its deposited form, and as there is always a large excess of this element in the hearth of every furnace, it seems unlikely that it should be powerless for perfect reduction, unless assisted by such minute quantities of cyanogen as frequently cannot be exceeded among the constituents of the materials under treatment.*

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* Since the above was in type another furnace at the Clarence Works has been set at work. The results afforded by it are also corroborative of the inference that the alkaline cyanides do not perform any very important office in the reduction and carburization of iron.

The first running after laying on the blast was ...	...	...					White iron.
Twelve succeeding runnings were	...	...	...	...			No. 3 ,,
Six ,, ,,	1-5th, No. 2; 4-5ths, No. 3;				average	...	,, 2·8
Four ,, ,,	2-3rds ,, 2; 1-3rd ,, 3;				,,	...	,, 2·33
One ,, ,,	almost all	...	...	...			,, 1·

Thus, on the second day after commencing to blow, foundry iron was produced; on the ninth day, No. 2 was run; and on the fourteenth day, No. 1, by which day the furnace was doing three-fourths of its full work, and consuming as little coke per ton of iron, as other furnaces which had been some years at work. It is evident, the accumulation, as regards alkaline cyanides, previously described, could not have gone to an extent likely to affect the products. During the time the blast was on, 20cwts., at the outside, of potash and soda together would have come down before the tuyeres, accompanied by about half this weight of cyanogen. Looking at the weight of iron made, this would not give above 3 lbs. of Cy per ton of metal, from which must be deducted about one half for that portion shown to be carried off in the escaping gases. It must be admitted, however, that it is by no means impossible that a small quantity of alkali may serve as a vehicle for conveying successive portions of Cy to act as a deoxidizing agent; just as certain compounds of N and O in the sulphuric acid chambers are the means of oxidizing large quantities of SO_2, by absorbing O from atmospheric air and conveying it to fresh portions of sulphurous acid. The whole subject is one upon which my mind is by no means made up, and will be resumed hereafter.

SECTION XXVII.—"FUME" EMITTED BY THE BLAST FURNACE.

In any very accurate account which might be framed with the view of assigning to every step involved in the operation of iron smelting, its own portion of heat absorption, an appreciable quantity would possibly fall to the share of those dense white clouds which float over many iron-making localities, and in particular over that engaged in reducing the Cleveland ore.

I am aware it has been suggested that this vapourous-like matter is merely extremely minute particles of earthy and other substances carried away by the force of the blast. There are many circumstances connected with its emission inconsistent with such a supposition. The only material used in the furnace likely to emit a white powder is the lime, but then this earth has been found to constitute only about two per cent. of the mass. The fuel affords, in many cases, a white ash, but inasmuch as the coke is burnt where fusion, and not mechanical expulsion, will prevail, this explanation of a source of the emanation in question is also unsatisfactory. Moreover, its composition and that of coal ashes do not agree, and if it were otherwise there are good reasons for believing that the "fume" or "flue dust," as it is called, may considerably exceed in weight the ashes in the fuel consumed.

Again, did this fume owe its origin to a mere mechanical action, it ought to be found chiefly among the gases in the upper part of the furnace. This is not so, it pervades every zone, and further is most plentiful when the greyest iron is being produced; showing evidently some connection between its copious formation and high temperature.

Assuming this substance to consist of its component parts which were expelled from the blast furnace by having at one time been in state of vapour, the question arises have they passed from the solid to the gaseous state by the mere force of heat. Looking at the silica and alumina present, both capable of sustaining such high

temperatures without change, this seems highly improbable. As much as 17 per cent. of zinc oxide has been detected in the fume. This probably is derived from the zinc being reduced in the hotter region of the furnace, volatilized and reoxidized when it is traversing the zone rich in CO_2. In like manner it is possible that silica, alumina, lime, &c., are deoxidized in the region of highest temperature by carbon or iron, or it may be by potassium or sodium; are then volatilized and share the same fate as the zinc, viz., oxidation. In this manner it is conceivable that aluminium or silicon, as a vapour, absorbing oxygen, may be in such a fine state of mechanical division as almost to resemble a true case of direct sublimation.

The fume itself readily condenses upon any solid matter exposed to it, and hence the necessity of periodically cleaning the hot air pipes fired with the waste gases. The same cause would lead one to expect a greater emission from a small furnace than from a large one, the increased column of material through which the gases pass intercepting a larger proportion than a shorter column. This appears to be so; for I found upon two occasions 77·31 and 59·09 parts were given off from a furnace 48 feet high, against 27·24 and 19·54 parts from a furnace 80 feet high; both estimated upon the same quantity of iron made.

In the flues along which the fume travels, certain portions condense. To avoid any irregularity of composition from this cause I erected a steam pump and drew through a foot or two of water the gases from a furnace 60 feet in height. The condensed matter was analyzed by M. Henri Brivet in the Washington laboratory. It contained—

Soluble in water.

Loss in heating	10·46	
SiO_2	1·37	
Al_2O_3	12·20	
CaO	tr.	
MgO	tr.	
Cl	·57	
SO_3	·59	
ZnO	4·58	
K_2CO_3 and Na_2CO_3	22·90	
	———	52·67

Soluble in water		52·67
Insoluble in water.		
SiO_2	11·00	
Al_2O_3 and Fe_2O_3	10·76	
CaO	2·06	
MgO	tr.	
ZnO	13·28	
CO_2	7·00	
Alkaline salts	3·07	
		47·17
		99·84

Thus, in round numbers, we may consider that the white clouds leaving our furnaces consist half of matter insoluble in water. Now, in five different experiments on the escaping gases (experiments 449 to 503), the smallest quantity of soluble matter was estimated to be 14·78 grammes per mêtre of gas. Of soluble and insoluble there would, therefore, be double this, or 29 grammes. This, upon 4,500 cubic mêtres of gas, the estimated bulk for each ton of iron, would give about 2·6 cwts. of fume per ton of metal produced.

These figures have been given rather to indicate a field for further enquiry, than from any great reliance to be placed on their accuracy, for it is evident that when such dissimilar results are obtained, a greater number of observations are required, than I have had time to bestow on the subject.

I have now completed the task I proposed to myself of endeavouring to explain the properties of those agents, by the instrumentality of which the various steps in the process of reduction and carburization of iron in the blast furnace are accomplished. Such an investigation must be regarded as an indispensable preliminary to the enquiry indicated by the title of the present work. The various experiments which have been described as illustrative of the subject, are mere selections of a much greater number, all undertaken with the view of satisfying myself of the truth of the general conclusions it has been my aim to lay down. Those, performed to ascertain the nature of the action of CO and CO_2 on other metals than Fe, may appear to some extent

superfluous; but the light they afford in forming an opinion respecting the character of the rëaction itself, when iron is employed, appeared to me to justify their insertion. I shall now proceed in an attempt to prove how the properties of the agents involved in the smelting of iron, taken singly, and in connection with each other, determine the capacity of the blast furnace, the temperature of the air, and the proper condition of the materials to be operated upon.

SECTION XXVIII.—ESTIMATE OF THE QUANTITY OF HEAT REQUIRED IN THE PROCESS OF IRON-SMELTING.

The practical question proposed for consideration in the few introductory remarks made at the outset of this enquiry, was stated to be the economy of fuel in smelting iron, as the same may be affected by the size of the furnace and by the temperature of the blast.

I now propose to endeavour to show, by a reference to the experimental researches described in these pages, how this very important question is regulated by the properties of those substances employed in, or produced by, the process itself.

The assistance afforded by the information contained in the preceding sections will be supplemented by additional evidence, derived in part from the laboratory, and in part from an appeal to the actual work performed by the blast furnace.

In such an investigation as the one now contemplated, there are two subjects which present themselves for examination. First, the actual heat required for the process; and, second, the manner in which this heat is obtained.

The heat required consists of that really absorbed by each stage of the operation and of loss. The former, if correctly stated, admits of no diminution; the latter, unless that emitted by the molten iron and slag in the act of cooling is susceptible of being utilised, does not promise any great margin for economy.

With regard to the generation of the heat, much misapprehension may result from any comparison of the entire heat-producing power of the fuel, with that actually afforded by the combustible matter burnt in a blast furnace.

One hundred parts of carbon converted into carbonic acid with air at 0°C. (32°F.) will give—

$$100 \times 8{,}000 = 800{,}000 \text{ heat units.}$$

Judging from a very large number of analyses, it would not appear that the average composition of the gases emitted by the blast furnaces in the North of England ever much exceeds 30 vols. of CO_2 to 70 of CO. From carbon so oxidized, the heat evolution is:—

C to CO_2 30	× 8,000	= 240,000
C to CO 70	× 2,400	= 168,000
Total	...	408,000 heat units.

or 51 per cent. of the quantity capable of being afforded by burning the whole of the C to CO_2.

The behaviour of oxides of iron, and that of the metal itself have been sufficiently dwelt upon to demonstrate the fallacy of computing the power of the fuel in a blast furnace upon the supposition that it can all be resolved into CO_2. We must, therefore, content ourselves with ascertaining to what extent the carbon, at the disposal of the iron smelter, can be made to assume its maximum state of oxidation.

The study of this question will form the matter of a separate section having for its object the investigation of the modes in which heat is produced in the blast furnace, for, previous to describing how this heat is generated, I propose endeavouring to ascertain the quantity actually required in the operation.

(A.) This varies to some extent, according to circumstances; but, for the purpose of illustration, an example will be selected of a furnace having a capacity of 11,500 cubic feet, smelting calcined Cleveland ironstone, yielding 41 per cent. of pig iron (about No. 3 in quality), and using 13·66 cwts. of limestone, per ton of metal. The temperature of the blast was 485°C. (905°F.), and that of the escaping gases, 332°C. (630°F.).

The sources of heat absorption will be divided under two classes, viz., those really required for the process, comprising chemical action and fusion,—and those which may be regarded as actual, although, to a great extent, unavoidable loss, so far as the operation in the furnace itself is concerned.

The methods pursued to determine the various values of the heat requirements will be given in the following section.

Most English chemists now employ the French scale in calculating the development of heat, *i.e.*, each heat unit is represented by one gramme (15·432 grains) of water raised one centigrade degree (1·8F.). The British ironmasters, however, being more familiar with tons and cwts. than with smaller quantities, and it being a matter of indifference what is selected for unity, I have adopted the cwt., which has, besides, the advantage of dealing with smaller numbers.

TABLE OF HEAT ABSORPTION.

Class I. Chemical action and fusion :—

		Cwts.				
No. 1.	Evaporation of water in coke, ·58 cwt. ...	·58	×	540	= 312	units
„ 2.	Reduction of 18·6 Fe from Fe_2O_3 ...	18·6	×	1,780	=33,108	„
„ 3.	Carbon impregnation ...	·6	×	2,400	= 1,440	„
„ 4.	Expulsion of CO_2 from $CaCO_3$	13·66	×	370	= 5,054	„
„ 5.	Decomposition of do....	1·64	×	3,200	= 5,248	„
„ 6.	Do. H_2O in blast H	·08	×	34,000	= 2,720	„
„ 7.	P.S and Si reduced from P_2O_5 SO_3 SiO_2 ...				4,174	„
„ 8.	Fusion of pig iron ...	20·0	×	330	= 6,600	„
„ 9.	Do. of slag ...	30·4	×	550	=16,720	„
					75,376	„

Class II. Loss regarded as chiefly unavoidable :—

„ 10.	Transmission through walls of the furnace	3,658	
„ 11.	Carried off in tuyere water ...	1,818	
„ 12.	Do. in gases	11,043	
			16,519 „
			91,895 „

The heat development at the furnace, which furnished the data from which the preceding table was in part compiled, was as follows:—

Oxidation of carbon (given hereafter)	81,536
Contributed by blast	11,919
	93,455

The close correspondence between the two sides of this account, the difference being only 1,560 units, must not be accepted as evidence of absolute correctness of the various numbers made use of in the computation. Indeed, there are one or two items entirely neglected, such, for example, as the absorption of heat by the expansion of the air, from the state of compression to which it is brought by the action of the blast engine. Again, there is some escape of heat from the bottom of the furnace into the earth, of which we have no account. This is equivalent to a slight understatement; but, on the other hand, the heat of the escaping gases is a little in excess, because they contain a certain quantity of heat, derived from the ironstone, not accounted for in the sum of that developed. The probable extent of this will be explained hereafter.

Assuming the amount of heat generated to be correct, viz., 93,455 units, we shall not, in all probability, be far from the truth in adopting—

Class I., as it stands in the table		75,376
Class II., corrected as follows:—		
Transmission, as before	3,658	
Tuyere water do.	1,818	
Gases, 2,496 units allowed for heat in the ironstone, &c.	8,860	
Expansion of blast, loss from hearth, &c., constituting the difference between the two sides of the account	3,743	18,079
		93,455

The total number of heat units absorbed in the production of one ton of iron varies, as a matter of course, with the circumstances attending its manufacture. The ironstone may, by its comparative poverty in metal, give rise to a greater quantity of slag, requiring

fusion, and an increased consumption of limestone, from this cause, is accompanied by larger volume of CO_2 to be reduced to CO. Again, the size of the furnace may be such as to permit an excessive loss of heat in the escaping gases.

All the causes of difference, just enumerated, are susceptible of being measured, and after this is done, and proper allowance made, the residual quantity of heat for the same quality of iron—say No. 3—should, in every case, be the same.

I propose to select instances of furnaces working under very dissimilar circumstances, and after eliminating the sources of difference, to contrast the residual numbers obtained by this mode of treatment.

It cannot be expected, from the nature of the enquiry, that perfect coincidence in the results should obtain; but, in order to judge of the precautions taken to ensure correctness, I will shortly describe the method pursued, in order to procure the data upon which the estimates are based.

Samples of the escaping gases were collected over three or four hours, and sufficiently often (six or eight times) to justify the inference that, in composition, they represented an average of those emitted by the furnace under examination. This precaution was absolutely necessary, owing to the fluctuation in the relative quantities of their constituents. The specimens were aspirated into a tube, containing about 30 to 40 cc.s, and sealed up under the blowpipe immediately after being filled, the current being maintained through the tube until all air was displaced. The samples, so procured, were submitted to analysis in the manner described in a previous section of these pages.

The quantity of coke consumed, per ton of iron, being known, it was easy to estimate with sufficient accuracy the actual quantity of carbon it represented. In like manner, from the known consumption of limestone, the weight of C derived from this source was computed.

The relation between carbon, in the form of CO and CO_2, and nitrogen being ascertained by analysis, the weight of blast and of gases escaping from the furnace, per ton of produce, were then calculated.

Formerly,* the method of estimation consisted in deducting from the carbon burnt to CO_2 that contained in the limestone, and excluding from the body of the calculation the heat absorbed by the reduction of the CO_2 contributed by the Ca CO_3 to Co.

It simplifies, perhaps, the formula, by considering all the CO_2 introduced in combination with Ca O, as escaping in the form of CO, and estimating all the remainder of the carbon also as producing CO. Such portion of this CO as analysis indicates to have been converted into CO_2 gives rise to a further generation of heat, and is estimated separately.

Upon the previous occasion referred to, ·74 cwts. of carbon was considered to be taken up by the iron. Further trials induce me to think ·60 cwts. to be nearer the truth, and, instead of regarding 8·14 cwts. of oxygen to represent that afforded by the ore for each ton of metal, I have assumed pig iron to consist of—

Fe	...	18·60 cwts.	representing	O as	Fe_2O_3	...	7·97	cwts.
P	...	·30 „	do.	„	P_2O_5	...	·39	„
S	...	·02 „	do.	„	SO_3	...	·03	„
Si	...	·48 „	do.	„	SiO_2	...	·55	„
C	...	·60 „						
		20·00					8·94	

This statement of 8·94 cwts. of oxygen, derived from the ironstone, presupposes that none of the bases, supposing they are earths, in combination with the three acids, P_2O_5, SO_3, and SiO_2 are decomposed. Now, Ca as Ca S, certainly, is found in the slag to a trifling extent, but still in sufficient quantity to give off SO_2 as it flows from the furnace, and to generate H_2S, when water is thrown on it. By the decomposition of the earths themselves, this 8·94 oxygen might be raised to near 9·5 cwts., and I have, therefore, taken 9 cwts. as the possible weight furnished from the ore.

The heat units, evolved by C to CO, are taken at 2,400; and by C to CO_2, at 8,000.

The computation of heat development (81,536 units) was founded

* Transactions of the Iron and Steel Institute, 1869.

upon the following volumetric examination of the furnace gases:—

Exp. 512. Hour of Sampling.	CO_2	CO.	H.	N.
1 p.m.	12·4	25·4	1·6	60·6
2·10 „	10·	28·1	·9	61·0
2·40 „	12·5	27·2	·8	59·5
3·45 „	10·6	26·8	·5	62·1
4· „	10·9	25·6	—	63·5
4·10 „	12·5	25·3	·5	61·7
4·20 „	12·9	28·8	·7	57·6
Average	11·7	26·7	·7	60·9
Av'ge of Duplicate Analyses,	11·75	26·62	·7	60·93

From these figures the composition by weight was reckoned te be—

Composition of Gases.		Carbon.	Oxygen.	Nitrogen.
CO_2	17·30 =	4·72	12·58	
CO	25·20 =	10·80	14·40	
H	·10			
N	57·40			57·40
	100·00	15·52	26·98	57·40

The hydrogen is in such trifling quantity that its presence may be neglected—that estimated to be due to the moisture in the blast is alone retained.

	Carbon in coke and limestone.
Coke used per ton of iron, 22·32 cwts., less ash, &c., 1·92 = C	20·40
C in limestone 1·64, carrying off an equal weight ($CO_2 + C = 2\,CO$)	1·64
	22·04

Leaving C burnt to CO ... 18·76 × 2,400 = 45,024
C of this CO burnt to CO_2 6·52 × 5,600 = 36,512

81,536

Gases, weight per ton of iron:—

Total carbon in coke and limestone ...	22·04 cwts.
Less taken up in iron	·60
Weight of carbon in gases	21·44

		Carbon.	Oxygen.
Nitrogen (15·52 : 57·40 :: 21·44)	79·30		
Carbonic acid	23·89 =	6·52 ...	17·37
Carbonic oxide	34·81 =	14·92 ...	19·89
Water in coke	·58		
H in moisture of blast	·08		
	138·66	21·44	37·26

Blast, weight of:—

Nitrogen, as above	79·30
Oxygen with do.	23·70
Moisture	·74
	103·74 cwts.

Comparing the total oxygen, per ton of iron, with that due to the various sources, we have:—

Total oxygen per ton of iron		37·26 cwts.
Oxygen brought in by blast	23·70	
„ by moisture ...	·66	
„ by ore	9·00	
„ by limestone ...	4·37	
		37·73
Difference for experimental error, &c.... ...		·47

The heat contributed by the blast, which had a temperature of 485°C. (905°F.) was—

103·74 cwts. × 485°C. × ·237 S. heat = 11,919 units.

The heat in the gases, for strict correctness, requires each substance to be calculated separately, which is done below, but, as the variation is inconsiderable, ·24 will be adopted in the succeeding cases.

N	79·30 cwts.	·243 SH =	19·270
CO_2	23·89 ...	·216 ...	5·160
CO	34·81 ...	·245 ...	8·528
H	·08 ...	3·409 ...	·272
H_2O as steam ...	·58 ...	·48 ...	·278
	138·66		33·508

Average specific heat ... ... $\frac{33·508}{138·66}$ = 0·2416.

From the actual number of heat units in the gases, a deduction will be made, representing, roughly, the supposed quantity of heat brought in by the materials. The temperature of the gases was 332°C.

Hence—138·66 cwts. × 332° × ·24 SH =	11,043	
Less, heat communicated by ore, &c. =	2,496	
		8,547
Latent heat of steam, 540 units × ·58 cwts. ...		313
		8,860

The following calculations contain the results obtained, by a similar mode of procedure, from four other furnaces working under circumstances entirely different from those just given :—

(B.) Furnace 48 feet high, 6,000 cubic feet, Clarence Works. Coke, 28·92 cwts. per ton of No. 3 iron; limestone, 16·00 cwts. Temp. blast, 485°C. (905°F.) Escaping gases, 452°C. (846°F.) Smelting calcined Cleveland stone.

		Total C in Coke and Limestone.
Coke used per ton of iron, 28·92 cwts., less ash, &c. ... ... 2·56 = C 26·36		
C in limestone 1·92, carrying off an equal weight ($CO^2 + C = 2\,CO$) ... 1·92		28·28
Leaving C burnt to CO ...	24·44 × 2,400 = 58,656	
C of this CO burnt to CO_2 ...	5·47 × 5,600 = 30,632	
		89,288

Gases, weight per ton of iron :—

Total carbon in coke and limestone	28·28		
Less taken up in iron	·60		
Weight of carbon in gases ...	27·68		
Nitrogen (16·29 : 57·6 : : 27·68)	97·87	Carbon.	Oxygen.
Carbonic acid	20·05	5·47	14·58
Carbonic oxide	51·82	22·21	29·61
Water in coke	·74		
H in moisture of blast	·11		
	170·59	27·68	44·19

Blast, weight of:—

Nitrogen, as above	97·87		
Oxygen with do.	29·23		
Moisture	1·02		
	——	128·12	
Comparing total oxygen, as before. There is per ton of iron			44·19
Oxygen brought in by blast ...	29·23		
„ by moisture ...	·91		
„ by ore	9·00		
„ by limestone ...	5·12	...	
	——		44·26
Difference for experimental error			0·07

(C.) Two Ormesby furnaces, 76 feet high, 20,642 cubic feet; coke, 22 cwts. per ton—Nos. 3 and 4 iron; limestone, 12·50 cwts. —using Cleveland ore. Temperature of blast, 780°C. (1,436°F.) Gases, 412°C. (774°F.):—

	Composition of Gases by Weight.		Carbon.		Oxygen.		Nitrogen.
Exp. 514.	CO_2 ...	16·00 ...	4·36	...	11·64		
	CO ...	29·50 ...	12·64	...	16·86		
	H ...	0·10					
	N ...	54·40 ...	—	...	—	...	54·40
		100·00	17·00		28·50		54·40

		Total C in Coke and Limestone.
Coke used, 22·0; less ash, &c., ...	1·66=20·34	21·84
C in limestone, 1·50; carrying off equal weight ($CO_2 \times C = 2\,CO$)	1·50	
C burnt to CO	18·84 × 2,400=45,216	
C of this CO to CO_2	5·45 × 5,600=30,520	
Total heat units from C to CO and CO_2		75,736

Gases, weight per ton of iron:—

Total C in coke and limestone ...	21·84 cwts.	
Less taken up in iron	·60	
Weight of C in gases	21·24	

		Carbon.	Oxygen.
Nitrogen (17·00 : 54·4 : : 21·24) ...	68·00		
Carb. acid	20·00 =	5·45	14·55
Carb. oxide	36·90 =	15·79	21·11
Water in coke	·57		
Hydrogen from blast	·07		
	125·54	21·24	35·66

Blast, weight per ton of iron :—

Nitrogen, as above	68·00		
Oxygen therewith	20·31		
Moisture	·63		
		88·94	
Comparison of oxygen, as before, in gases ...			35·66
Brought in with blast	20·31		
„ with moisture do. ...	·56		
„ with ore	9·00		
„ with limestone ...	4·00		
			33·87
Difference for experimental error			1·79

In this case, it seems probable, the coke was a little understated.

(D.) Consett: furnace, 55 feet high, 9,400 cubic feet; coke, 22·75 cwts. per ton of No. 4·97 iron; limestone, 8·25; Cleveland ore and hæmatite, 48 per cent. Temp. of blast, 454·5°C. (850°F.) Gases, 477°C. :—

	Composition of Gases by Weight.		Carbon.	Oxygen.	Nitrogen.
Exp. 515.	CO_2 ...	14·70	= 4·01 ...	10·69	
	CO ...	29·30	= 12·56 ...	16·74	
	H ...	·10			
	N ...	55·90	... ...	...	55·90
		100·00	16·57	27·43	55·90

		Total C in Coke and limestone.
Coke used, 22·75 cwts., less ash, &c., 2·04=... C	20·71	21·70
C in limestone, ·99, carrying off equal weight (CO_2+C=2 CO) ...	·99	

C burnt to CO ... ... 19·72 × 2,400 = 47,328
C of the CO to CO_2 ... ... 5·11 × 5,600 = 28,616

Total heat units from C to CO and CO_2 ... 75,944

Gases, weight per ton of iron:—

		Carbon.	Oxygen.
Total C in coke and limestone ...	21·70		
Less taken up in iron	·60		
Weight of C in gases	21·10		
Nitrogen (16·57 : 55·9 : : 21·10)	71·17		
Carb. acid	18·71	= 5·11 ...	13·60
Carb. oxide...	37·31	= 15·99 ...	21·32
Water in coke	·59		
Hydrogen in blast	·08		
	127·86	21·10	34·92

Blast, weight per ton of iron:—

Nitrogen, as above	71·17		
Oxygen therewith	21·26		
Moisture	·70		
		93·13	
Comparison of oxygen.—In gases ...		... ...	34·92
Brought in by blast	21·26		
„ moisture do. ...	·62		
„ ore	9·00		
„ limestone	2·64		
			33·52
Difference for experimental error ...		... ...	1·40

(E.) Consett: furnace 55 feet high, 10,300 cubic feet; coke, 18·00 cwts. per ton of No. 4·16 iron; limestone, 8·12; Cleveland ore and hæmatite ore, 48 per cent. Temp. of blast, 718°C. (1,324°F.) Gases, 248°C. (478°F.)

Composition of gases by weight.			Carbon.	Oxygen.	Nitrogen.
Exp. 516.	CO_2 ...	17·5 ...	4·77 ...	12·73	
	CO ...	28·1 ...	12·04 ...	16·06	
	H ...	·1			
	N ...	54·3			54·30
		100·0	16·81	28·79	54·30

		Total C in coke and limestone.
Coke used 18·00, less ash, &c. 1·62=C	16·38	17·35
C in limestone	·97	
C burnt to CO	15·41 × 2,400	=36,984
C of this CO burnt to CO_2	4·75 × 5,600	=26,600
Total heat units of C to CO and CO_2		63,584

Gases, weight per ton of iron:—

Total C in coke and limestone ...	17·35			
Less taken up in iron	·60			
Weight of C in gases	16·75			
Nitrogen (16·81 : 54·3 : : 16·75)	54·10	Carbon.		Oxygen.
Carb. acid	17·43	= 4·75	...	12·68
Carb. oxide	28·00	=12·00	...	16·00
Water in coke	·45			
Hydrogen in blast	·07			
	100·05	16·75		28·68

Blast, weight per ton of iron:—

Nitrogen, as above	54·10	
Oxygen therewith	16·16	
Moisture	·81	
		71·07

Comparison of oxygen. In gases ...	...	...	28·68
Brought in by blast	16·16		
„ moisture do. ...	·72		
„ ore	9·00		
„ limestone	2·59		
	——	...	28·47
Difference for experimental error ...	...	...	·21

The annexed table has been constructed from the data just given, so as to give, at one view, the actual quantity of heat absorbed for the work done in the five preceding furnaces. This is obtained by taking the sum of the heat units generated by the oxidation of the carbon, and contributed by the blast—and deducting from it those carried away in the gases.

PARTICULARS.	A. Clarence.	B. Clarence.	C. Ormesby.	D. Consett.	E. Consett.
Height of furnace in feet	80	48	76	55	55
Cubic capacity in feet	11,500	6,000	20,642	9,400	10,300
Materials used—					
Coke per ton of iron, in cwts ...	22·32	28·92	22·00	22·75	18·00
Ironstone do. do. ...	48·80	48·80	48·80	41·67	41·67
Limestone do. do. ...	13·66	16·00	12·50	8·25	8·12
Weight of blast per ton iron, in cwts.	103·74	128·12	88·94	93·13	71·07
Escaping gases do. ...	138·66	170·59	125·54	127·86	100·05
Temperature of blast, in deg. Cent....	485	485	780	454·5	718
Gases ... do.	332	452	412	477	248
Heat evolved by oxidation of carbon, in cwt. heat units	81,536	89,288	75,736	75,944	63,584
Contributed by blast	11,919	14,724	16,439	10,528	12,081
Total heat generated in furnace, units	93,455	104,012	92,175	86,472	75,665
Less heat carried off in gases*	8,860	16,409	10,213	13,839	5,095
Leaving for furnace work	84,595	87,603	81,962	72,633	70,570
*Deducted from gases for heat communicated by materials, units ...	2,496	2,496	2,496	1,100	1,100
Units added to do. for latent heat of steam from H_2O of coke	313	399	308	319	243

For the purpose of proper comparison, all sources of heat absorption, which differ in the five cases just given, should be eliminated, and thus, there will remain over, a sum which may be designated as one of *constant requirement.*

These differences are:—

(a.) Weight of slag to be melted, varying with richness of ore.

(b.) Weight of H_2O decomposed, affected by volume of blast employed.

(c.) Weight of CO_2 expelled from limestone, varying with quantity of $CaCO_3$ used.

(d.) Decomposition of CO_2 of $CaCO_3$, arising from the same cause as in (c.)

(e.) Evaporation of H_2O in coke, varying with weight of coke used, and its hygrometric state.

TABLE OF CONSTANT REQUIREMENTS.

	A. CLARENCE.			B. CLARENCE.			C. ORMESBY.			D. CONSETT.			E. CONSETT.		
Height of furnace, in feet	80			48			76			55			55		
Capacity of do. in cubic feet	11,500			6,000			20,642			9,400			10,300		
Materials used per ton of iron, in cwts	Coke.	Ore.	Limestn.	Coke.	Ore.	Limestn.	Coke.	Ore.	Limestn.	Coke.	Ore.	Limestn.	Coke.	Ore.	Limestn.
	22·32	48·8	13·66	28·92	48·8	16·00	22·00	48·8	12·50	22·75	41·67	8·25	18·00	41·67	8·12
Temperatures, degrees, Centegrade	Blast 485.		Gases 332	Blast 485.		Gases 452	Blast 780.		Gases 412	Blast 454½.		Gases 477	Blast 718.		Gases 248
Heat units left for furnace work, as per statement			84,595			87,603			81,962			72,633			70,570
Elimination of variable sources of absorption.*															
(a) Fusion of slag	16,720			17,710			16,335			10,550			10,450		
(b) Decomposition of H_2O in blast ...	2,720			3,740			2,380			2,720			2,380		
(c) Expulsion of CO_2 from Ca CO_3 ...	5,054			5,920			4,625			3,052			3,004		
(d) Decomposition of CO_2 do. ...	5,248			6,144			4,800			3,168			3,104		
(e) Evaporation of H_2O in coke	313			399			308			319			243		
			30,055			33,913			28,448			19,809			19,181
Diff. being constant requirement of furnace ...			54,540			53,690			53,514			52,824			51,389

*(a) Weight of slag in cwts., at 550 units per cwt.	30·40		32·20		29·7		19·2		19·0	
(b) H in H_2O of blast ,, 34,000 ,, on H ...	·08		·11		·07		·08		·07	
(c) Weight of limestn. ,, 370 units per cwt.	13·66		16·00		12·50		8·25		8·12	
(d) Weight of C in do. ,, 5,609 ,, ,,	1·64		1·92		1·50		·99		·97	
(e) ,, H_2O in coke ,, 540 ,, ,,	·58		·74		·57		·59		·45	

On running the eye over the greatly dissimilar factors, which all terminate in numbers, having quite as close a resemblance as the nature of the calculation permits us to expect, there seems strong reason for believing that the division of the heat requirements, as well as their sum, is not far from being correctly set forth.

SUMMARY.

Clarence	... 80	feet furnace	...	54,540	heat units.
do.	... 48	do.	...	53,690	do.
Ormesby	... 76	do.	...	53,514	do.
Consett	... 55	do.	...	52,824	do.
do.	... 55	do.	...	51,389	do.
Average	...	...	...	53,191	do.

—representing a coëfficient of constant requirement.

In respect to these numbers, 54,000 units may be taken as the figures representing constant requirement; to which must be added 30,000, for the other items mentioned under the head of variable amounts. As regards the Consett furnaces, the iron produced being of a lower quality, about Nos. 4·97 and 4·16, instead of No. 3, the difference is, probably, easily accounted for upon principles which will be mentioned hereafter.

In compiling the estimates, which have just formed the subject of examination, the amount of heat development has been founded upon the quantity of CO_2 actually existing in the gases as they escape.

It would, perhaps, be more correct in principle, although it would not affect the result, to deduct from the quantity of C burnt in the hearth to CO—that portion of carbon which has been gasified by CO_2 formed by reduction of the Fe_2O_3 and carbon impregnation. The quantity of CO_2, due to these causes, has been considered equal to 6·58 cwts. per ton of iron, and, indeed, as much as 6·52 cwts., as CO_2 was actually present in the first instance given.

In this latter mode of dealing with the figures, we should, of course, have to regard the 6·58 cwts. as affording heat due to its conversion, in the first place, to CO_2; and then credit the absorption account with the change of the C in CO_2 to CO, which has disappeared, as shown by the final quantity of carbonic acid found in the gases.

In the 48 feet furnace, instead of 6·58 C as CO_2, we had 5·47, equal to 1·11 cwts. less C as CO_2 than might have been present:—

1·11 C heat development from CO to CO_2	$1·11 \times 5,600 =$	$+6,216$
1·11 C less in hearth, forming CO ...	$1·11 \times 2,400 =$	$-2,664$
		$+3,552$

—against which has to stand the heat absorbed by reducing 1·11 C from the state of CO_2 to CO ... ... $1·11 \times 3,200 = -3,552$

leaving the balance unaffected.

SECTION XXIX.—RESPECTING THE MODES EMPLOYED TO ASCERTAIN THE HEAT-ABSORPTION OF EACH STAGE OF THE OPERATION.

At the beginning of the previous section, the sum of the heat units required in the smelting of iron was divided among twelve distinct steps or stages of the process. The united amount was shown to correspond very closely with the number of heat units developed by the quantity of carbon and oxygen existing in the escaping gases, added to that contained in the blast.

In dealing with such large weights as are treated in the blast furnace, it is extremely difficult to state precisely the weight of coke consumed; and, if we knew the quantity, to be sure of its composition, as regards carbon, ash, and moisture, would be all but impossible. The same observation is applicable to the flux and ore consumed, and still more difficult would it be to state with absolute precision the actual average composition of the gases which leave the furnace. It is upon the data furnished by these two sets of observations, that the number of heat units evolved in the blast furnace is calculated, and it is only after the performance of a great

number of experiments, in which error probably corrects error, that the smelter is safe in laying down a formula for his own guidance.

Having ascertained the heat development, we now come to consider its appropriation, as set forth in the twelve divisions formerly enumerated; and it becomes necessary to explain upon what authority the figures, previously specified, are obtained, which investigation will furnish matter for the present section.

No. 1. *Evaporation of Water in Coke.*

The heat absorption, when water passes into the state of steam, varies according to different writers, from 536 to 540. The latter number has been adopted.

No. 2. *Absorption by* $Fe_2 O_3$, *in Reduction of* 18·6 *cwts. Fe.*

Taking pig iron to contain 7 per cent. of carbon, silicon, &c., one ton will represent 18·6 cwts. of Fe.

According to Dulong, whether a given weight of oxygen, united with CO, or with Fe, the result was about the same in heat development.* One litre of the gas giving 6,216 units with the former, and 6,260 with the latter.

In two sets of experiments, no indications were obtained of there being any rise in the temperature when CO was passed over $Fe_2 O_3$, at moderate temperatures.

Exp. 517. Seventy grammes of calcined Cleveland ore were introduced into a large test tube, and immersed in an oil bath, and heated to 225°C. Atmospheric air, warmed by being passed in a bent tube, also heated by the oil bath, was conducted through the ore. The temperature, as indicated by a thermometer placed in it, showed a fall of 5·5°C. CO was now used instead of common air, when a similar decrease was observed, the gases, in both cases, being no doubt somewhat cooler than the ore, and the increase of temperature, if any, in the case of the CO, being too minute to be observed.

Exp. 518. In two observations at a temperature of 315°C., there appeared an increase of 1° in passing CO over pure $Fe_2 O_3$, but in two others, when the thermometer stood at 318°C., no rise was noticed.

In both these experiments there was sensible reduction, but the heat evolved was too small to give sufficiently marked results.

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*Transactions of the British Association, 1845, page 166.

According to more recent investigations, Dulong's conclusion has been confirmed to the extent that the balance of heat evolved, over that absorbed, is very small. Unfortunately, however, we do not possess sufficient data to be able to estimate the heat produced by the union of three equivalents of oxygen with two of iron, because, in burning the metal in this gas, Fe_3O_4 is formed, and not Fe_2O_3. According to Andrews, one of Fe so oxidized gives out 1,582 units, whereas, one of CO burnt to CO_2 affords 2,431 units of heat.

In the equation $Fe_3O_4 + 4\,CO = 3\,Fe + 4\,CO_2$, we have 84 of iron, and 56 of CO.

56 CO to CO_2	× 2,431 =	136,136	calories evolved.
84 Fe from Fe_3O_4	× 1,582 =	132,888	do. absorbed.
	Balance ...	3,248	do. for heat evolved.

which is only equal to 39 units of heat for 1 of Fe.

Admitting, however, the probability that the extra quantity of oxygen in Fe_2O_3, as compared to that in Fe_3O_4, evolves heat by its union with the metal, and that this extra quantity is proportionate to the additional oxygen, we have—

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2$$

in which there is 56 of Fe and 42 of CO.

42 CO to CO_2 ...	× 2,431 =	102,102	calories evolved.
56 Fe from Fe_2O_3	× 1,582 =	88,592	„ absorbed.
	Balance ...	13,510	for calories evolved.

Or 241 calories per unit of Fe reduced.

According to Andrews, the heat evolved by burning Fe to Fe_3O_4 is 1,582 units; and if the union with iron of the additional quantity of oxygen found in Fe_2O_3 is accompanied by a corresponding heat development, the number of units set free would be 1,780.

Under these circumstances, it seems highly probable that the heat absorbed by the reduction of 18·6 cwts. of Fe from Fe_2O_3 will be somewhere between—

	18·6	×	1,582	... 29,425
and	18·6	×	1,780	... 33,108

I have accepted the latter number, in every case, as the basis of calculation, as being, most probably, the nearest the truth.

No. 3. *Carbon Impregnation.*

When carbon is deposited by the dissociation of CO, (2 CO=C+ CO_2,) one of carbon of the CO is burnt to CO_2, evolving 5,600 units; and one of C in CO is unburnt, absorbing 2,400. The former number is accounted for in the calculations of heat development, being a portion of the C in the CO_2—formed by the oxidation of the CO. The other number finds its place among the items of heat absorption.

No. 4. *Expulsion of CO_2 from Limestone.*

This was found by Mons. Ser to be 370 calories per unit of Ca CO_3. This number has been accepted without further experiment, because it corresponds pretty fairly with the experience of the blast furnace obtained by the use of lime, from which about two-thirds of the CO_2 has been expelled by previous calcination. The saving of coke by this preliminary roasting is about ¾ cwt., which may be taken to represent 3,000 cwt. heat units, or 4,500 units, were all the CO_2 expelled. If these were divided over 12 cwts. of limestone, we have 375 units, which is almost exactly that given by Mons. Ser.

No. 5. *Decomposition of CO_2 in Limestone.*

The quantity of C. in 13·66 cwts. Ca CO_3 is 1·64 cwts. When this carbon, in the form of CO_2, escapes, it is resolved into CO, by carrying with it a similar amount of C from the fuel.

The heat change attending this re-action $CO_2+C=2$ CO is as follows:—

1 of carbon in CO_2 reduced to C absorbs	...	8,000 units
2 of C burnt to CO evolves $2\times2,400$	...	4,800 „
Balance for absorption	...	3,200

The heat afforded by burning the carbon of the coke being accounted for here, must be, and is subtracted from the total C burnt in the hearth.

No. 6. *Decomposition of H_2O in blast.*

This source of absorption, owing to the ever changing quantity of moisture in the atmosphere, is liable to considerable fluctuation. In the case selected for examination, ·74 cwts. of H_2O are considered present for each ton of iron, and this being equal to ·08 cwts. of hydrogen, we have $·08\times34,000$ (units evolved by H burnt to H_2O) equal to 2,720 units.

The prejudicial effect on the furnace, of a very moist atmosphere, has been long known to iron smelters, but I do not remember having met with any account in which the injury from actual experience was reduced to figures.

By the kindness of my friend, Mr. James Hunter, of the Coltness Ironworks, near Glasgow, I have received data which enable me to give the information in this form. The furnaces in question being situate in a damp climate on the West of Scotland, must generally be working with a blast pretty highly charged with moisture, but during the recent very severe winter this state of things was considerably modified. The unusually hard frost would free the atmosphere, in a great measure, from aqueous vapour, and, no doubt, in consequence, produced the marked saving of coal experienced generally during its continuance over all the twelve furnaces of this establishment.

In the moist months of the autumn, 1870, the average consumption of raw coal was about 3·50 cwts. more than during two months of the frosty weather. According to Kämtz's table of atmospheric moisture, it is quite possible that the air at Glasgow might contain in the autumn as much as 1 per cent. of water. Roughly, the weight of blast at the Coltness works will be about 140 cwts. per ton of iron, so that as much as 1·4 cwt. of water would be injected into the furnace for this weight of metal. Now, 1·4 H_2O is equivalent to ·155 H and ·155 × 34,000 units gives 5,270 units absorbed by this quantity of H_2O reduced to H. Of the 3·5 cwts. of coal, only the coke it contains would be burnt in the hearth, and as this coal contains 65 per cent. of coke, the 3·5 cwts. of coal represents 2·27 cwts. of fuel which would reach the lower part of the furnace. This addition to the quantity of fuel required by the ordinary purposes of the furnaces would, of course, only be burnt to CO, so that, inclusive of the heat contained in the blast, it would only furnish about 3,000 units per cwt. of coke. Having gained, as formerly stated, 5,270 units, we have 5,270 ÷ 3,000* = 1·75 cwts. of

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* The extra carbon burnt in the hearth would probably all escape as CO heat per unit.

From this, we have	2,400	cwt. heat units.
Heat in blast, say	600	do.
	3,000	

coke, equivalent to 2·69 cwts. of raw coal. The difference (3·5 – 2·69) ·81 cwts. of coal may be due to the hot air stove fires burning better, and to the diminution in volatile matter of the fuel which had to be expelled. Under any circumstances the difference is not a large one, and the general result is sufficiently well marked to merit notice.

No. 7. *Phosphorus, Sulphur, and Silicon.*

These elements are derived from the deoxidation of P_2O_5, SO_3, and SiO_2. According to Andrews, P, burnt to P_2O_5, evolves 5,747 units.* M.M. Troost and Hauteville state, that they have determined that the union of Si with O, to form SiO_2, is accompanied with the generation of 7,830 units. Monsieur Jordan makes the number nearer 8,000, from observations of his own on the oxidation of Si in the Bessemer steel process. † Of sulphur to SO_3, I possess no information; burnt to SO_2, 2,220 to 2,300 may be assumed as the evolution of heat units. I have taken 2,500 as representing S to SO_3, but whatever the number may be, the error must be of small importance, owing to the mere trace of sulphur present.

The numbers are as follows, per ton of iron :—

·30	Cwts. of	P	reduced from	P_2O_5,	·30 × 5,747 = 1,724	
·30	„	Si	„ „	SiO_2,	·30 × 8,000 = 2,400	
·02	„	S	„ „	SO_3,	·02 × 2,500 = 50	
						4174

Nos. 8 and 9. *Fusion of Pig Iron and Slag.*

Mons. Vathaire‡ ascertained by means of the liquifaction of ice that one part of No. 3 pig iron, as it ran from the furnace, gave out 330 calories. It being difficult to obtain a continuous series of observations on iron, which is only run out twice in the 24 hours, I performed a great number of experiments on the slag as it flowed from the blast furnace, to learn how nearly my own figures coincided with those of this gentleman, whose investigations pointed to 550 calories being contained in one of slag, when the furnace was running No. 3 iron.

Exp. 519. An ordinary calorimeter was used in the first instance. An iron crucible, 1½ inch diameter and 3 inches long, was filled with melted slag, weighing about 220 grammes, and transferred imme-

* Watt's Dictionary of Chemistry, Article on Heat.

† Societé des Ingenieurs Civils Séance du 18 Mars, 1870.

‡ Etude sur les hauts fourneaux.

diately to the calorimeter. The quantity of ice melted was then ascertained.

A second plan consisted in immersing a piece of malleable iron, weighing about 570 grammes, in the current of slag, until it acquired the temperature of the stream, and then transferring it to the calorimeter. The iron being partially fused, was weighed after the experiment, and allowance being made for difference of specific heat between it and the slag, the calories in the latter were estimated accordingly by the weight of ice which was converted into water.

The mean of the experiments tried with the calorimeter gave as high a number as 572 calories, but as there would be a certain amount of ice melted by absorption from the atmosphere, I have adopted the number obtained by Mons. Vathaire, both for iron and slag.

No. 10. *Transmission of heat through walls of furnace.*

On a previous occasion,* I described, by means of a drawing, the apparatus employed for ascertaining this source of heat absorption. It consisted of a copper vessel holding 19 litres of water, and surrounded on all sides but one by an air space of two inches. With the exception of this one side, the whole was covered by three or four layers of flannel, which, with the air space, prevented loss of heat communicated to the water during the experiment. When the instrument was used, it was placed tightly against the furnace, with the exposed surface about half an inch from the side of the building, this distance being preserved by means of a wooden frame covered with vulcanised indiarubber and flannel, corresponding to the edge of the air space. The elastic nature of the latter prevented any passage of currents of air between the exposed copper surface and the furnace. The apparatus was filled with water, and the amount of heat it absorbed during a given time was carefully noted.

In the case of the Wear furnace, built of fire bricks and held together by iron hoops, it was estimated that, on an average, 4,900 square feet emitted

55·4	kilogs.	units	per	superficial	foot per hour, equal to	271,460
450	square	feet,	118	units	per foot per hour, „	53,100
321	Do.		151·25	„	„ „	48,551
					kilogramme units	373,111

* Transactions of Iron and Steel Institute, 1869.

This is equivalent to 7,316 cwt. heat units per hour for two tons of iron produced during this time, or 3,658 cwt. units per ton.

The results thus obtained cannot be regarded as rigidly correct, because the conditions during the observation are not identical with those which obtain under ordinary circumstances. The proximity of a mass of cold water to the furnace may abstract heat more slowly or more quickly than the atmosphere, according as the latter is in a quiet or agitated state. The quantity of heat given off by the casing will alter somewhat as the water in the instrument approaches the temperature of the outside of the furnace, and from the nature of the apparatus, all loss by convection is arrested. The total quantity, however, according to my experiments, which escapes by transmission, is not such as to render the probable difference one of any importance, for it does not amount to 5 per cent. of the whole heat developed.

So far as I recollect, the only other attempt which has been made to ascertain the extent of loss by transmission through the walls of the blast furnace is in a book, which has already been referred to in these pages, viz.: "Dokumente betreffend den Hohofen zur Darstellung Von Roheisen," by M. Karl Schinz, of Strasburg, and since then translated by Messrs. Maw and Müller.

The work in question contains a number of experiments on subjects connected with iron smelting, exceeding by far those in any other production of a similar nature, and will remain a monument of the patience and assiduity of its author. Notwithstanding the confidence expressed by M. Schinz, in his preface, in his own views, I regret to be unable to adopt the conclusions as even approaching to correctness arrived at by so industrious a fellow-labourer as he appears to be.

In illustration of this, I may refer to pages 49 and 123, of the translation, in which, not by direct experiment, but by adopting the analyses of Ebelmen, M. Schinz makes it appear that in the case of the furnace at Clerval, 69 per cent., and in that of the furnace at Séraing, 50 per cent. of the total heat developed is lost by transmission.

To ascertain the heat really evolved by such a method of computation, the quantity of CO and CO_2 produced per unit of iron should be ascertained. To this the heat communicated by the blast must be added, and by deducting that carried off by the

gases, we have the net amount absorbed during the process in the manner already explained in these pages.

At Clerval, 100 parts of C as CO escape with something like 34 parts as CO_2; and at Séraing, 100 of C as CO with about 25 of C as CO_2.

In both M. Schinz's estimates he puts down half the consumed carbon to produce CO_2, instead of observing the above proportions, and adds nothing for heat in the blast in either case. No account is taken of any loss by the escaping gases at Clerval, and, in my opinion, that at Séraing, which appears only to be surmised, is greatly understated.

Under these circumstances, it is not extraordinary that his quotient bears no analogy to the actual truth. There are other fallacies in M. Schinz's mode of computation which it is not necessary to dwell on, seeing the manifest mistake which will be apparent to any one on being assured that one-half the heat generated in a blast furnace is supposed to be lost through the walls.

I would further observe, that were the loss from transmission considerable, it ought to be greatly affected by those circumstances which are known to influence conduction, radiation, and convection; such as proportion of surface for a given amount of work, and thickness of wall through which the heat has to escape.

At the Clarence Works, there are furnaces of different capacities in which the surface bears to the 24 hours' make of iron, widely different proportions, and it happens, as might be expected, that the walls, for stability's sake, are strongest in the larger furnaces. The following statement gives the thickness of walls of furnaces smelting the same materials, and shows the relative area of surface calculated upon the make of each furnace.

Furnace containing	Relation of surface to make of iron.	Thickness of cone walls.	Thickness of wall of boshes.
11,500 cubic feet reckoned as unity	1·	3 ft. 7 in.	4 ft.
15,500	·959	... 4 ft. ...	4 ft.
25,500	1·104	4ft. 9in.	5 ft. 6 in.

I possess no means independent of my own experience of knowing what amount of difference would be produced by furnaces working under circumstances so various as regards facility for transmission of heat through their walls. With these conditions so much altered, it strikes me as indisputable, that, were the loss from this

cause considerable, the consumption of coke could not fail to have been affected, which is contrary to my experience.*

No. 11. *Heat carried off by tuyere water.*

It was ascertained, that from five tuyeres and the tymp, 20,250 litres (equal to 397 cwts.) of water ran per hour, and that this quantity had its temperature raised 9·16°C. (16·5F°.) This is equal to 3,436 cwt. units; and taking the make at 2 tons for the time in question, we have 1,818 units per 20 cwt of iron.

No. 12. *Sensible heat escaping in the gases.*

Two sets of experiments are required for this—first, the composition of the gases themselves, and second, their temperature. Both are liable to great fluctuations, as was incidentally mentioned in Section IX., and will be found alluded to in Section XXXII.

In the case which served as a basis for the calculation now being made, viz., that of an 80 feet Clarence furnace, seven samples were taken, and each formed the subject of two examinations in the manner already described.

The very convenient electric pyrometer of Mr. Siemens permits a series of observations to be taken with very little trouble, and as it only requires about ten minutes for the instrument to acquire the temperature of the gases, its indications may be relied on. By means of this apparatus, I have a series of readings taken every ten minutes over eight consecutive hours upon different days, and I am able by this experience to confirm the figures which formed the basis of calculation in my former estimates.† I shall have occasion in a future section to make use of the figures thus obtained, so that more need not be said on the subject at present.

There is one disturbing cause which it is difficult to appreciate correctly, viz., how far the heat brought in by the materials affects the temperature of the escaping gases. I have sometimes imagined in a furnace of 12,000 cubic feet this might, on an average, amount to 100°C. In two furnaces at Ferryhill, one of 16,000 and the other of 33,300 cubic feet, the gases were going off at both, at about

* A moderate fall of rain falling on the iron casing of the furnace of 25,500 cubic ft. maintains a continuous wet surface of 50 feet from the top; and the water collecting together runs over the next 15 feet in separate paths, probably more than half being evaporated on the way, and the remainder drops from a projection on the building. As an example of the extreme slowness with which the heat passes through fire brick, a wall 5 feet thick forming the well of a furnace was at work for many weeks before its temperature measured by holes drilled in the sides became stationary.

† Transactions of Iron and Steel Institute.

190°C. (374°F.), whereas, at all the Clarence furnaces, they were nearly 166°C. (300°F.) above this. Thinking the moisture in the ironstone might account in part for this, I have in the estimates contained in the previous Section, only deducted 75° in a furnace smelting hot Cleveland ore, and giving off 138·66 cwts. of gases—which is equivalent to (138·66 × 75° × ·24 SH) 2,496 cwt. heat units, which is deducted when smelting hot calcined ore.

The correction in the case of a furnace using a large proportion of cold and partially moist hæmatite would be less than this, and I have, therefore, assumed that the hot calcined ironstone only communicated 35°C. to the gases, which amounts to about 1,100 cwt. units.

So far as the real question at issue is concerned, the final result is not much affected by the doubt attending this latter part of the enquiry.

The quantity of heat produced by the combustion of the fuel in the preceding estimates is based upon accepting C burnt to CO, evolving 2,400 units, and C to CO_2, 8,000. According to other experiments, 2,221 and 7,900 are nearer the truth, and these were the numbers I formerly adopted.*

In the present work, the former figures have been made use of, as they appear to be those more generally quoted in writings on heat, but I am not aware that any experiments of a sufficiently conclusive character have proved that the one set rather than the other is the more correct. It is, indeed, just as probable that the truth may lie between the two extremes.

This subject is alluded to for the purpose of pointing out that the application of the smaller numbers, in calculating the heat development, would so reduce the heat units generated by the combustion of the fuel, that the balance of 3,743 units, inserted as due to expansion of the blast and other causes, would be unnecessary. On the other hand, this lesser amount of heat produced by the oxidation of carbon would, unless the reduction of $Fe_2 O_3$ absorbs a smaller quantity of heat than has been assumed, which is very possible, convert this latter action into a cooling process from one of an opposite character, which appears to me contrary to the observed facts. If we have to admit a change in the quantity of heat absorbed by the deoxidation of the iron oxide, this would diminish the absorption

* Transactions of Iron and Steel Institute, 1869.

just as altering the factors of heat development would lessen the other side, and thus a descrepancy between the two sides of the account would still remain.

Which ever class of figures constitutes the basis of computation, the final result will not be affected beyond a mere trifle. It will be admitted that a knowledge of the actual quantity of heat required in the process of smelting is not an unimportant subject of study for the ironmaster, and if we obtain this within the probable limits of error contained in the preceding estimates, some advance has been made in our acquaintance with the laws which regulate the important branch of metallurgical science, which it is the object of this work to investigate.

SECTION XXX.—ON THE ORIGIN OF THE HEAT PRODUCED IN THE BLAST FURNACE.

In Section XXVIII., an attempt was made to ascertain, with as much correctness as possible, the actual amount of heat necessary for performing the required duty in the blast furnace. This was done by summing up the number of heat units considered to be absorbed at every stage of the smelting process. The amount so obtained was then contrasted with the actual heat supposed to be generated within the furnace, and the two sides of the account were found to agree as closely as the nature of the estimate admitted. The same mode of procedure was then adopted with four other furnaces working under very different circumstances, and in these also, the heat production and the heat appropriation were found to correspond in a similar manner. As an additional check upon the method of computation pursued, after certain differences were eliminated from the account, the five furnaces thus examined presented a result in which the extreme amount of difference (3,151 units) was considerably under that represented by one cwt. of coke as it is burnt in the blast furnace.

In the Section referred to, the various sources of the heat generated were incidently spoken of, viz.:—

1. The direct oxidation of the fuel by the blast and its conversion into CO.
2. The further oxidation of a portion of the CO, formed as above, by the ore under treatment leading to the production of CO_2.
3. The heat of the blast.

A little further consideration of these three divisions will be of use in the present enquiry.

A vast number of changes no doubt occurs among the constituents which fill a blast furnace during the descent of the column of solid matter into the hearth. Until the fuel, which for the present is considered to be coke, becomes sufficiently heated after being charged, it may be regarded as entirely inert, except to the extent to which it intercepts the heat swept upwards by the escaping gases.

When the coke reaches a temperature of 410°C. (770°F.), *Vide* Exp. 446, it no doubt begins to act slowly on the CO_2 found in large quantities in this region of the furnace. This decomposition of carbonic acid increases as the temperature rises to which it is exposed when it meets C, Fe, or Fe_xO_y. At a lower level, where the materials are red hot, the CO_2 contained in the limestone is given off, and will be rapidly resolved into CO.

Down to the point where the materials are now supposed to have descended, deoxidation and carbon deposition will have progressed considerably, and, in consequence, the conflict among the five reactions described in Section XV. will have become very active. CO_2 once liberated will be reduced in part either by the coke, or more readily by carbon deposited in contact with the ore, by the reduction of which the CO_2 is generated. The same office may be in some degree performed by metallic iron, or by a suboxide (Fe_xO_y), and the CO resulting from the decomposition of the CO_2 may serve in another part of the furnace to reduce an oxide containing more oxygen than the Fe_xO_y which split up the CO_2.

So far, however, as final results are concerned, it is a matter of indifference how numerous these changes have been. The quantity of carbon consumed and the heat evolved being judged of by the final composition of the gases as they leave the furnace. It is more than probable, looking at the quantity of deposited carbon found in

the furnace, that a good deal of the coke itself is consumed before it reaches the tuyeres, and its place supplied by the former.

Actual analysis would demonstrate, as we might expect, that the quantity of carbon actually oxidized at the tuyeres is about the weight contained in the coke, less that portion which has been carried off by CO_2 ($CO_2+C=2\ CO$).

The case which served in Section XXVIII. as an illustration for ascertaining the heat development and appropriation in a furnace of 11,500 cubic feet was shown to contain 21·44 cwts. of carbon per ton of iron in the escaping gases. Upon another occasion, when working with the same quantity of coke, but emitting rather less CO_2, its gases at the tuyeres were made the subject of careful examination.

The quantity of solid carbon actually oxidized in the higher part of the furnace is considered to be that which is dissolved by CO_2, this acid being evolved by the limestone, or generated by reduction and carbon deposition.

Upon the occasion alluded to, the CO_2 in the limestone represented 1·52 cwts. of carbon, and, instead of 6·58 of C from reduction of Fe_2O_3 and dissociation of CO appearing in the gases, the quantity was only 5·52, leaving a deficiency of 1·06, which had also disappeared under the action of $CO_2+C=2\ CO$.

We have thus, from the C, actually in gases, viz., ...	21·44
to deduct 1·52+1·06, or	2·58
leaving to be burnt at the tuyeres ... ... cwts.	18·86

Exp. 520. The composition of the gases near the tuyeres, by volume, was—

CO_2	1·7
CO	35·0
H	0·3
N	63·0
	100.

So that, by weight, excluding the hydrogen, they contained—

CO_2	2·6 = carbon	...	·71
CO	34·7 = „	...	14·86
N	62·7		
	100·		15·57

In the present instance, the carbon in the escaping gases were associated with 75·53 of nitrogen. Their composition at the tuyeres gave 15·57 of C, with 62·7 of nitrogen, hence,

$$62{\cdot}7 : 15{\cdot}57 :: 75{\cdot}53 : 18{\cdot}75,$$

being the quantity of carbon actually burnt at the tuyeres, instead of 18·83, arrived at by the other method of computation. The cause of an excess will be spoken of hereafter.

Whether a portion of the blast at the moment of its entry into the furnace gives rise to the formation of a small quantity of CO_2 or not, is unimportant. The experiments of my friend, Professor Tunner, and the analyses recorded in Section II., would appear to indicate that the heat development in the hearth itself is that due to the burning of C to CO, so trifling and so momentary is the presence of carbonic acid.

The trials instituted to form an idea of the relative temperatures of different portions of the crucible mentioned in the Section just referred to, were repeated over many days at another furnace, with the following results:—

Exp. 521.	A Below Tuyeres 15 inches.	B Level of Tuyeres.	C Above 13 inches.	D Tuyeres 34 inches.
	C 238	189	202	227
	or F 440	374	396	440

Here, the coolest part of the lower portion of the furnace is coincident with the level where the air is admitted. Between this point and one 13 inches above, ought to be the area of maximum heat, if any great quantity of CO_2 is generated, for analysis proves that it is resolved into CO before it travels as far as C. But the temperature increases as we ascend towards D, no doubt owing to its removal from the point where the blast exercises a cooling influence. Had a trial further up the furnace been made, probably there would have been a further slight rise, inasmuch as the contents of the crucible itself appear to be somewhat hotter than those opposite D; at all events, the external temperature of the walls would indicate such to be the fact. Where a large volume of air is propelled among heated carbon, the rapidity with which it becomes saturated with this element—in other words, becomes converted into carbonic acid—must necessarily depend on the intimacy of the contact between the blast and the carbon.

M. Schinz, in his experiments recently mentioned,* seems to have bestowed infinite trouble to ascertain the effect of area of contact by reducing his fuel to spheres of different sizes (20, 30, and 35 millimetres diameter), and then by burning these separately, in layers of from ·062 to ·186 mêtres in thickness, he obtained the character of the combustion by analysing the resulting gases. The translators of M. Schinz's book point out a very great and obvious error in the mode adopted by this author for estimating the "free spaces" interposed among spheres when laid together; but omitting this correction, M. Schinz estimates that each cubic mêtre of air blown into a furnace per second requires one square mêtre of contact for the formation of carbonic acid, and 12 square mêtres of contact for the reduction of this acid into carbonic oxide.

So far as the blast furnace is concerned, I would submit, these troublesome experiments are useless, because the area of contact in iron smelting between the blast and carbon is almost infinite, not from the surface presented by the coke which is consumed in the hearth, but from the air meeting on all sides the deposited carbon in so fine a state of division as to render perfectly intelligible the correctness of Mr. Tunner's explanation and the error of M. Schinz in supposing the primary effect of the blast meeting carbon in the furnace to be the formation of CO_2. In the instance adopted for illustration in the preceding Section, the total heat units from the combustion of the carbon in CO is $18{\cdot}76 \times 2{,}400$, or 45,024 cwt heat units.

The second source of heat has its origin in the conversion of a portion of the CO generated in the manner just described into CO_2 by the action of the oxide of iron. Assuming each ton of iron to contain 18·6 cwts. of Fe, the quantity of oxygen united with this quantity of iron is 7·97 cwts. The C required to convert 7·97 O into CO is 5·98, and the heat evolved by raising one of C in the form of CO to CO_2 is 5,600 units: hence the reduction of the iron for one ton of pig is accompanied by the generation of $5{\cdot}98 \times 5{,}600 = 33{,}488$ units.

Besides this mode of heat generation, there is another arising from the deposition of carbon dissolved in the iron. This will, of course, depend in amount on the quantity of C found in the iron, due to

* Dokumente betreffend den Hohofen zur Darstellung von Roheisen.

the action of $2CO=C+CO_2$. In the case under consideration, one ton of metal is deemed to contain ·60 cwts.:

We have, therefore,—·6 C burnt to $CO_2 = ·6 \times 8{,}000 = 4{,}800$ calories.
less $2 \times 0·6$ C as CO reduced to C, $2 \times 0·6 \times 2{,}400 = 2{,}880$ "

1,920

In the production of iron containing ·6 cwts. per ton, the maximum quantity of carbon existing in the gases as CO_2 is 5·98 + ·6 or 6·58 cwts., and the total heat development will be 36,848 units. According to the analysis of the gases in the example upon which the heat absorption per ton of metal was estimated, the carbon in this state of oxidation was 6·52 cwts., and the calories 36,512. The trifling difference, only ·06 cwts., between calculation and actual results may be due to experimental error, or the disappearance of this small quantity of carbon, as CO_2 may arise from its having been reduced to CO by carbon. This, of course is, in point of heat development, the same thing as if this ·06 cwt. had never passed from the state of carbonic oxide to that of carbonic acid, and is attended with the additional inconvenience of carrying off a similar weight of carbon from the furnace also as CO. This reaction, when it takes place to any extent, is an undoubted defect in the mode of conducting the process, but it will be more convenient to pursue its examination when the performance of furnaces of various capacities forms the subject of discussion.

The third source of the heat produced in the blast furnace is that contained in the air propelled into its interior by the blowing engines.

In all estimates of heat evolution, the calories are calculated upon the supposition of the blast being furnished at 0C. (32°F.) In the severest weather, the temperature of the air as it leaves the blast cylinder, from the compression it has experienced, always exceeds this.

Taking a furnace using cold air, consuming two tons of coke to a ton of iron, and receiving its air at 40°C. (104°F.), which is a common temperature after compression in the blast cylinders, the following would be something like the number of heat units it would receive from this source.

The weight of air required for the combustion of 40 cwts. of coke, would be about 210 cwts., and this heated to 40° (210 cwts. ×

40° × ·237SH), is equal to 1,990 units. The proportion of heat thus afforded to the general fund is exceedingly trifling, being under two per cent. of the whole in the case of a cold blast furnace.

The ratio between the number of calories developed by the combustion of the fuel, and those contained in the blast in furnaces blown with hot air, may vary considerably according to circumstances, and the same may be said of the extent to which the carbonic oxide is converted into carbonic acid. This is best seen by a reference to the heat units derived from each source in the examples, which, in Section XXVIII., served as the means of demonstrating the heat development and appropriation in five different furnaces. The following statement presents a synopsis of the sources of heat in each of these cases, the numbers given being cwt. heat units.

Smelting iron.	Clarence 80 feet furnace. Clev. stone. No. 3 & 4.	Clarence 48 feet furnace. Clev. stone. No. 3 & 4.	Ormesby 76 feet furnace. Clev. stone. No. 3 & 4.	Consett 55 feet furnace. Clev. stone. and red ore. No. 4.	Consett 55 feet furnace Clev. st. and red ore. No. 4·9
Blast ...	485°C	485°C	780°C	454·5°C	718°C
Coke per ton	22·32	28·92	22·00	22·75	18·00
C to CO ...	45,024	58,656	45,216	47,328	36,984
Blast ...	11,919	14,724	16,439	10,528	12,081
CO to CO_2	36,512	30,632	30,520	28,616	26,600
	93,455	104,012	92,175	86,472	75,665

Which numbers furnish per 1,000 units the following proportions:

C to CO ...	482	564	490	547	489
Blast ...	128	141	178	122	159
CO to CO_2 ...	390	295	332	331	352
	1000	1000	1000	1000	1000

SECTION XXXI.—ON THE EXTENT TO WHICH THE HEAT PRODUCED BY THE COMBUSTION OF THE COKE CAN BE REPLACED BY THAT CONTAINED IN THE BLAST.

The present might be a convenient opportunity of endeavouring to take into account the nature of the conditions which confer a value upon the use of heated air in smelting iron, and at the same time of studying the circumstances which marked its introduction as one of the most important inventions in metallurgical practice. The examination of the operation of the blast furnace involves, as we have seen, two or three questions, such as the temperature of the air, that of the gases, and the composition of the latter. It is almost, if not quite, impossible to enter upon one of these without being brought into the presence of one or both the others. This difficulty meets us, as it has done before, upon the present occasion, and hence it will be more convenient to postpone any attempt to explain the mode of action of the hot blast, until further enquiry into the action of the furnace itself, renders such an explanation more easy to give and more easy to understand.

We must content ourselves now with an admission, which will not be disputed by any ironmaster, that the use of heated air is advantageous in point of economy, due to the fact, if to nothing else, that the heat units so obtained are generated either by a fuel cheaper than that used in the furnace, or in many cases by the escaping gases, which, if not so applied, would render them in fact what they are now happily not—waste gases.

Until within the last dozen years, partly owing to the danger of destroying the metal pipes constituting the hot air apparatus, and partly from an idea that there was little benefit derived from heating the blast above the point capable of melting lead (327°C., 620°F.), this was the temperature which pretty generally satisfied the minds of furnace managers. The Cleveland ironmasters were, I believe, among the first who attempted generally something

beyond this, and in a short time no one in their district was content unless zinc fused (which it does at 417°C., 782°F.), in half-a-dozen seconds when placed in the blast pipe.

The advantage of this additional heat soon made itself apparent, and then still higher limits were sought by the furnace-owners on the banks of the Tees. Unfortunately, the use of cast iron pipes presented a barrier to much further progress in this direction, although I do not consider a temperature equal to that of fusing antimony (450°C., 842°F.), with proper care, to be beyond the power of this description of apparatus.

I was early impressed with the desirability of being independent of this structural defect in this mode of heating air, and I undertook a series of experiments in which, by communicating a high temperature to various substances, the heat so accumulated was subsequently swept out, as it were, by the current of air to be heated. I was so engaged when Mr. Cowper patented Mr. Siemens' idea of what he calls his regenerative system to the hot air stoves. This, as is well known, consists in alternately heating masses of brickwork, and passing the air to be heated through them. The most sanguine expectations were at once formed of what, at one time, was considered almost an unlimited power of heating the blast, and it was maintained upon several occasions that the same economy which had attended the first and subsequent additions to the temperature of the air, would be realized by means of this new form of apparatus. Some of the advocates of the use of very highly heated air, who promised a proportionate saving of fuel for every 100° in the temperature of the blast, omitted, as I formerly pointed out,* taking into their calculations the diminished quantity of air required, as the fuel burnt at the tuyeres becomes reduced in quantity. This change of conditions imposes, of course, on a lessened volume of air, the duty of conveying the heat represented by the hundred degrees in question. In other words, as less air is required for the smaller quantity of coke, a given number of heat units conveyed into the furnace by the diminished amount of air greatly raises the temperature of the latter.

An exact estimate framed for showing the rate at which this increase of temperature progresses, requires certain corrections,

* Transactions Mechanical Engineers. Transactions Iron and Steel Institute.

because the less the fuel consumed per ton of iron, the less is the weight of the gases leaving the furnace. It by no means follows that the temperature of these gases will be the same with different quantities of coke, but as I possess no information to guide me, and as the disturbance owing to any deviation in this respect can only be slight, we will assume in each hypothetical case the products of combustion are leaving the blast furnace with a temperature of 330°C. (626°F.)

To constitute perfection of working, it is essential that CO_2 once formed in the reducing zone should escape as such, and the carbon in this form has been found frequently to exist, to the extent of 6·52 per ton of iron, 6·58 being regarded the full equivalent, this latter number will be considered as representing C in CO_2 generated by deoxidation and carbon impregnation.

Of course, so far as a mere matter of heat evolution is concerned, it is indifferent whether the C which finds its way into the pig iron is derived from the coke, or from the finely divided carbon with which the ore appears saturated.

As a question of fact, deposited carbon presents conditions so much more favourable for the union, that I feel persuaded we must regard it, rather than the coke, as the source of the ingredient in the metal.

The following tables are constructed to show what the composition of the gases will be, followed by a calculation of the estimated temperature of the blast, based upon the consumption of coke, from 22 down to 15 cwts. per ton of iron

The number in the table representing the sum of heat units absorbed per ton of iron, is compiled from the estimate given in Section XXVIII., allowance being made for the reduced quantity of limestone used in the present case, and less slag to be fused. Some trifling and variable amount should be deducted for the diminished quantity of blast, and therefore of moisture, which suffers decomposition. To cover all these differences, an average reduction of 2,455 units is made, leaving the actual number 91,000, of which 9,000 is regarded as representing sensible heat in the gases, and 82,000 that required for other purposes. In each case the estimated temperature of the blast is somewhat understated, probably about 80°C., (145°F.) because it is assumed that the full 6·58 cwts. of carbon, per ton of iron, escape as CO_2, which, in reality, is seldom the case.

We learn, then, from the information contained in the preceding statements, how rapidly the temperature of the blast rises when a constantly diminishing weight of air is made the vehicle of conveying a constantly increasing quantity of heat.

For the sake of clearness, the figures bearing on this question are extracted and placed side by side with the additional temperature estimated to be required to save each cwt. of coke named in the table:—

Coke, per ton of iron.	Weight of blast.	Heat units contained in blast. } =	Temperature of blast.	Additional number of degrees required for each successive cwt. of coke saved.
22 cwts. ...	106·17 ...	8,480 ...	337°C. ...	
21 „ ...	100·83 ...	10,332 ...	433 „ ...	96°C.
20 „ ...	95·43 ...	12,156 ...	537 „ ...	104 „
19 „ ...	90·08 ...	13,955 ...	654 „ ...	117 „
18 „ ...	84·35 ...	15,753 ...	786 „ ...	132 „
17 „ ...	79·39 ...	17,585 ...	935 „ ...	149 „
16 „ ...	74·00 ...	19,348 ...	1,103 „ ...	168 „
15 „ ...	68·65 ...	21,209 ...	1,304 „ ...	201 „

The escaping gases being now universally employed in the North of England as fuel in the hot-air stoves, it may be well to examine the calorific powers they possess.

The temperature produced by this gaseous combustible is that due to the oxidation of so much carbonic oxide, less the heat

Cwts.	Cwts.	Cwts.
17	16	15
11	11	11
17·00	16·00	15·00
1·27	1·20	1·12
15·73	14·80	13·88
1·32	1·32	1·32
17·05	16·12	15·20
·60	·60	·60
16·45	15·52	14·60
5·09	5·09	5·09

absorbed by the CO_2 and N, mixed with it after being burnt in the heaters or elsewhere.

Taking gas containing by weight the following constituents, neglecting H, and hydro-carbons,

CO_2	... ...	17·25
CO	... ...	25·25=10·82 of carbon.
N	... ...	57·50
		100·

the following exhibits its temperature of combustion :—

Weight of gas to be burnt, say	100·
Add weight of air required to burn 25·25 CO to CO_2	62·6
In addition to this, there is always a considerable excess of air over and above that required for complete combustion ; taking this at 20 per cent. of whole...	40·4
	203·

The temperature from this, taking SH at 24, is expressed by

$$\frac{10{\cdot}82 \times 5{,}600}{203 \text{ cwts.} \times \text{SH } 24} = 1{,}243°\text{C. } (2{,}270°\text{F.})$$

Independently, then, of any sensible heat contained in the gases themselves, and apart from any rise in the temperature of the combustion produced by the heat of the furnace in which ignition takes place, it is apparent this description of fuel is capable of producing any amount of heat the smelter is likely to require. At the same time it is very doubtful, unless by means of the use of enormous plant, whether anything approaching to the temperatures just mentioned, can be obtained by the fire brick stoves. At Consett, for example, at one furnace 36,726 square feet of surface is capable of raising 5,000 to 6,000 cubit feet of blast per minute, to about 600°C. (1,112°F.), and at another 43,558 square feet afford 4,000 to 5,000 cubic feet of blast, heated to a temperature of 740°C (1,364°F.) This is fully three times the superficial area employed in stoves of cast iron, heating something like the same quantity of blast to about 480°C. (896°F.)

This want of readiness on the part of fire brick in communicating its acquired temperature to the incoming air, is no doubt due to the indifferent conducting power of the material itself. Notwith-

standing the much larger surface thus rendered necessary in the form of apparatus under examination, it is a question for consideration, whether, looking at its indestructibility, it does not offer, independently of other circumstances, certain advantages. This matter was debated at a meeting of the Iron and Steel Institute, in May, 1870, when I gave it as my opinion, that so far as a mere matter of cost of plant and working were concerned, it might be slightly in favour of the Siemens-Cowper heater.

Our present object, however, is neither with the full extent to which air is capable of being heated by any particular form of apparatus, nor with the relative economy of those of brick and those of iron, but with the actual value of what I formerly distinguished by the name of superheated blast.*

From what has preceded, we may regard the process of reduction and carbon deposition as one effected by the solvent power possessed by carbonic oxide over oxygen. This power has no limit short of entire saturation—*i.e.*, the perfect conversion of the CO into CO_2 when the needful oxygen is free, and is not interfered with in its combination with the carbonic oxide, by the reactions which we have seen accompany the splitting up of an iron oxide.

At the present moment, we will content ourselves with assuming that something like 45 Vols. is the maximum quantity of CO_2, which a furnace can carry along with 100 Vols. of CO, which, in point of fact, assumes that 6·58 cwts. of carbon per ton of iron may be contained as CO_2 in the gases of a furnace working on calcined Cleveland ironstone. I will now proceed in an attempt to prove that the instant we seek to exceed the relative quantity of carbonic acid just named, a fresh state of conditions is established.

Let us examine the case of the Ormesby furnace, alleged, according to the table given in Section XXVIII., to be producing iron with 22 cwt. of coke and a total heat generation of 92,175 units, as compared with 93,455 units and 22·32 cwts. of coke at one of the Clarence furnaces of half its size. These figures will be accepted as the basis of calculation, although reasons were given at the time for thinking that the consumption of fuel at Ormesby was really a little more than that stated in the return.

In the estimates framed upon the analysis of the gases, 6·52 cwts. of carbon, per ton of iron, were shown to be leaving the furnace at

* Transactions, Iron and Steel Institute, 1869.

the Clarence Works, affording (6·52 × 5,600) 36,512 units. The blast, conveyed into the Ormesby furnace, per ton of iron, 16,439 units, whereas at the other, only 11,919 were derived from this source, showing a difference of 4,520 units. But mark the effect on the gases. Instead of 36,512 units having been obtained by the production of CO_2, only (5·45 × 5,600) 30,520 are due from this source at Ormesby, and, in consequence, the volumes of CO_2 per 100 of CO, instead of being as they were at Clarence, about 44, were reduced to 35 vols. The result of this change of circumstances is concisely stated at the end of the preceding Section, in which the relations of the different sources of heat are given for every 1,000 units actually evolved. At both works, those derived from the formation of CO are about the same, viz.: 482 and 490 units per 1,000. At Ormesby, however, 50 units more have been furnished by the blast, (178 instead of 128), and this is compensated for by the lesser quantity of CO at Ormesby, 332 instead of 390, having been oxidized to the state of CO_2. Now, this in reality means that whereas it is in our power to obtain these 58 units, free of all cost, from the more perfect combustion of our fuel *inside* the furnace, we refuse to do so, and supplement the loss by a corresponding number obtained by burning the very same quantity of CO *outside*, and returning the heat so generated in the hot air apparatus to the operation.

I have endeavoured, by a great number of researches, to determine at what point of admixture with CO_2 carbonic oxide ceased to affect calcined Cleveland ironstone exposed to its influence, at something like the temperature at which it leaves the blast furnace. Exps. 95 and 104 may be quoted as examples to show that the action was extremely feeble which took place when 100 vols. CO were diluted with 31 to 50 vols. CO_2. The power of the furnace itself to impregnate, as it were, the carbonic oxide generated by the combustion of the coke with oxygen has also been made the subject of investigation. This important question embraces the whole subject of fuel consumption, and will be resumed when the dimensions rendered necessary to ensure a proper period of contact between the ore and the reducing gas, forms the subject of discussion.

It is my intention to point out in the following two sections, by actual reference to the working of furnaces of different sizes, the dimensions which suffice to prevent waste from the loss of sensible heat in the gases, as well as to afford the CO

opportunity of taking up its full complement of O, and I am, therefore, almost tempted to close the present Section by simply pointing out how unlikely it is that the introduction of monstrous furnaces, driven with superheated air, can be attended with any benefit in respect to fuel, when we have just had an example of a furnace of 11,500 cubic feet, making 270 tons per week, with its blast at 485°C. (905°F.), with as little coke, and of as good quality (No. 3) as a furnace of 20,640 cubic feet, producing 440 tons with its air often heated to 780°C. (1,436°F.) Not only has this been clearly demonstrated, but the actual cause of difference, it appears to me, has been satisfactorily traced out. Now, the problem awaiting solution is, if doubling the dimensions and raising the temperature have been attended with the results just described, will increasing one or both of these again not be attended with precisely the same consequences as those which followed the first addition?

I am, however, induced to pursue the subject of super-heated air a little further, for, by the kindness of Mr. Jenkins, of the Consett Works, I have been furnished with some particulars bearing so directly upon the question at issue, and confirming so entirely the views laid before the Iron and Steel Institute upon former, as well as the present, occasions, that I cannot refrain from availing myself of the permission given by the proprietors of that establishment to assign them a place in these pages.

In 1869*, I communicated the results of certain observations on two furnaces at Consett, one using air at 454½°C., and the other having its blast at 718°C., and the account has been repeated in a preceding part of this work. I wish to draw attention to this last-named furnace, the results of which are to be found under the column E of the table. The gases escaped at 248°C. (478°F.), and the iron was made with 51,389 units, representing the coefficient of constant requirement compared with something above 54,000 at one of those at the Clarence works. The iron at the former furnace was lower in quality than that made at the Clarence furnace, which may account for the lesser absorption of heat at the latter. I will accept the number 51,389 as the true one, at Consett, and prove, notwithstanding this low amount of heat units, they were not the result of the best order of working, because, on comparing the sources of heat with those from the Clarence furnace

* Transactions of Iron Institute for that year.

of 11,500 cubic feet, it is found the oxidation of CO only furnishes 350 per 1,000 units at the former, against 390 at the latter, and that the blast furnishes almost the entire deficit. The actual figures in the resumé formerly given were—

	Clarence.	Consett.
CO	482	489
Blast	128	159
CO_2	390	352
	1,000	1,000

I have elsewhere pointed out that the Eston furnaces made pig iron with a consumption of coke almost the same as that at Consett using the superheated air. This was done when they were engaged in smelting the same mixture as that employed at Consett, viz., a mixture of hæmatite and Cleveland stone, but driven with air about the temperature of melting zinc as usually practised at Middlesbrough. I infer from this, having no analysis of the gases, that the advantage of the Eston furnace over those at Consett was owing to their burning more CO to the state of CO_2; indeed, there seems no other way of accounting for the difference.

At the period of my visit, the Consett company were engaged in constructing a furnace one-third larger, with Mr. Whitwell's modification of the Siemens-Cowper stove of one-fifth more surface than that which furnished the data for my previous estimates.

The following figures show the respective sizes and conditions of the two furnaces using superheated air at the time they were visited a second time, and both smelting the same mixture of hæmatite and Cleveland ore as that used on the former occasion:—

	No. 4 Furnace.	No. 5 Furnace.
Height	55 feet ...	55 feet
Cubic capacity	10,300 ...	13,460
Temperature of blast ...	598°C. (1,107°F.)...	740°C. (1,364°F.)
Ditto escaping gas ...	196°C. (384°F). ...	197°C. (386°F.)
Weekly make of iron ...	464 tons ...	426 tons
Average quality No. ...	4·49 ...	4·47

Instead, however, of the larger furnace, with its blast 150°C. (270°F.), sometimes 220°C. (396°F.) higher than the smaller one, making its iron under more favourable conditions than its neigh-

bour, the very reverse was the fact. It made less iron, of an inferior quality, and this with a greater consumption of coke, ranging from 1 to near 2½ cwts. to the ton. At the same time, its escaping gases never exhibited a higher temperature, and, indeed, often were cooler, than those from the lesser furnace, presenting, as was pointed out to me, the apparent paradox of a larger heat production and absorption with worse results.

This anomaly, however, disappeared on an examination of the gases, which proved that the excess of heat contributed by the blast was accounted for by the inferior oxidation of the carbonic oxide.

On subjecting the gases to analyses, and calculating the heat absorbed, it was found that No. 4 furnace, so far as regards saturation with oxygen, was doing almost as well by receiving its blast at 598°C., as at 718°, which was the temperature upon the occasion of the previous examination. On the other hand, the larger furnace (No. 5) driven with air at 740°C. upon this occasion was performing its duty, not only in an inferior manner to No. 4, but also with a less amount of oxygen absorption than that found in the gases of this last-mentioned furnace when it was receiving its blast at 718°.

Underneath is given, at one view, the sources of the heat per 1,000 units taken from the three examinations, and prefixed by that of the Clarence furnace (Section XXX.)

	CLARENCE.	CONSETT.		CONSETT No. 5.
Cubic content	11,500 ft.	No. 4 containing 10,300 ft.		13,460
Temperature blast	485°C	598°C.	718°C.	740°C.
Division of heat				
From C to CO ...	482	500	489	511
„ Blast ...	128	150	159	184
„ CO to CO_2 ...	390	350	352	305
	1,000	1,000	1,000	1,000

Now, the most expensive source of heat is of course that given in the first line, viz., C to CO, which represents the fuel supplied to the furnace. Practically, we may assume that the heat arising from the direct combustion of the coke is the same in the first three cases.

The second line contains the units derived from the blast, and it will be seen the only effect of raising the temperature of the air from 485° to 718° has been to substitute so much blast-heat for so much obtained by a more complete oxidation of carbonic oxide.

The sums of the heat units contained in the last two lines in the examples afforded by the Clarence and the Consett No. 4 furnace are 518, 500, and 511, numbers which in such calculations may be regarded as almost identical. It will be perceived that a moderate temperature of blast, comparatively, in the Clarence furnace is accompanied by an evolution of heat (390 units) which, according to my views, is the maximum amount we can expect to realise from the oxidation of carbonic oxide in smelting Cleveland ore. As the quantity of heat carried in by the blast is augmented, that arising from the generation of CO_2 is lessened, having fallen away from 390 units in the first column to 352 in the third.

It cannot be pretended that this is an advantageous mode of working, for it simply means burning CO to CO_2 outside, and returning the resulting heat into the furnace, the blast being the vehicle. A much simpler process, of course, is to oxidise the CO by means of the ore and retain it in that condition, as happens when air of a moderate temperature is used in a furnace sufficiently large for its work.

The fourth column contains information by which it would appear the high temperature of the blast has resolved so much CO_2 into CO that the two together, instead of contributing about 515 units, only do so to the extent of 489, the deficiency being made up by those furnished by the combustion of coke. A still more serious cause of loss consists in a greatly diminished quantity of heat being due to the generation of CO_2, which now only appears to the extent of 305 per 1,000, instead of 390, as in the case of the more perfect oxidation of the gas at the Clarence furnace.

After a careful examination of the various circumstances in connection with the working of the furnaces at Consett, I suggested to Mr. Jenkins the advisability of reducing the temperature of the blast at No. 5, and according to the last information received from that gentleman, they are already experiencing some advantage from the change.

Without pledging myself to the absolute accuracy of all the preceding figures, because to do this would require many more analyses of the gases than I have had an opportunity of having made, it seems to me the character of the results points to one conclusion, viz., that there is a certain temperature for each part of the interior of a blast furnace, which is best suited to securing the

most perfect oxidation practicable of the gases, and that if this temperature in the upper part is exceeded, the superabundant heat is absorbed by a decomposition of carbonic acid. What constitutes this perfect state of oxidation will be taken up in the Section devoted to the saturation of CO with oxygen gas.

SECTION XXXII.—ON THE CAPACITY REQUIRED BY THE BLAST FURNACE TO AVOID UNNECESSARY LOSS FROM THE PRESENCE OF SENSIBLE HEAT IN THE ESCAPING GASES.

So far back as 1857, Mr. Parry* pointed out the advantage which was to be gained by enlarging a furnace from 4,200 cubic feet to 6,000 feet. He mentions that whereas, in the former, the gases escaped at 640°F., from the latter they issued at a temperature of 360°, and he reasoned that the 280° being carried down would be serviceable for the general purposes of the furnace. I do not remember meeting with any earlier account of attention being drawn to the loss which was occasioned by the presence of sensible heat in the escaping gases, in iron smelting. Mr. Parry gives no particulars of the means he employed to ascertain the temperatures mentioned above, which are very different from anything met with in the North of England. If, however, this addition to the capacity enabled Mr. Parry to reduce the temperature of the issuing gases to 360°, he was probably correct in supposing a maximum capacity to have been attained. No more heat, he considered, could be absorbed from the gases, and greater height might be attended with inconvenience from a crushing action on the fuel.

Both in Scotland and Wales much larger furnaces have been constructed, rather, I suspect, in the hope of making more iron, than in the expectation of saving fuel. None, however, gave satisfactory results, and either they were abandoned or no more were

* Transactions of South Wales Institute of Engineers, 1857.

built. The mode adopted of collecting the waste gases by means of the cup and cone, devised by Mr. Parry himself, afforded an opportunity of estimating the actual amount of heat carried off by a given quantity of gas, and the weight of the latter being ascertained by analysis, it was easy to calculate the total loss of heat units per ton of iron.

In the neighbourhood of Middlesbrough, we commenced with what Mr. Parry considered the maximum capacity a furnace ought to have, viz.: 6,000 cubic feet, and in the year 1862, I undertook, with such pyrometers as we then possessed, to ascertain the quantity of heat escaping from our blast furnaces.

From one making about 220 tons per week, the gases had a temperature of 450° to 460°C. (842° to 860°F.), and as much as upwards of 19,000 cwt. heat units per ton of iron left the throat of the furnace. In this case, the heat produced by oxidising the fuel was equal to 3,340 cwt. heat units per cwt. of coke, and the blast represented 510 units; or the coke and blast together, 3,850: so that the loss from this cause was that afforded by about 5 cwts. of coke. Upon another occasion, it was equivalent to 5·5 cwt. of coke, or about 18 per cent. of the whole fuel consumed.

Furnaces were gradually enlarged up to 60 feet, when, in the year 1862, Messrs. Bolckow and Vaughan erected one at Middlesbrough 75 feet in height, with a capacity of between 10,000 and 11,000 cubic feet, the gases from which I immediately made the subject of enquiry.

As might be expected, their temperature was found sensibly lower than that of those from the furnaces of 6,000 feet, but they still contained so much heat that, having occasion to erect two new furnaces at the Clarence Works, 80 feet was adopted, and boshes of 20 feet, with a capacity of nearly 15,500 cubic feet. Subsequently, still larger furnaces, viz.: 25,500 cubic feet have been built at this establishment, and others recently erected by Messrs. Cochrane have a cubic content of 43,000 feet, being 90 feet high, with boshes of 30 feet.

The instruments employed eight years ago were not such as enable me to speak with certainty as to the exact temperature possessed by the gases; but whatever error there existed, was probably shared by all alike, and, therefore, does not materially affect the argument. Since the period at which these trials were

made, Mr. Siemens has described a pyrometer, the indications of which are obtained by measuring the varying amount of resistance of a platinum wire exposed to the heated medium, and through which an electric current is made to pass. This instrument was described by Mr. Siemens himself, to the members of the Iron and Steel Institute, and has been extensively employed by me in more recent experiments.

It must be remarked that there are many circumstances which interfere greatly with the regularity of temperature exhibited by the gases as they are emitted from a blast furnace. The ironstone brought from the kilns is more or less highly heated, and the coke may contain a greater or less quantity of water, both of which circumstances exercise a sensible influence on the temperature of the gases. To these disturbing causes another must be added, viz.: the extreme fluctuation in the character of the action going on in the furnace itself, which will materially affect the quantity of heat actually evolved at different times.

An instance of great irregularity in the composition of the escaping gases is exhibited in the following analyses, performed upon specimens collected from a furnace smelting Cleveland stone :—

Exp. 522. Composition at	12·40 p.m.	1·0 p.m.	1·30.	2·30.	3·30.
CO_2	28·6	11·9	10·5	10·8	11·2
CO	19·6	29·9	31·3	31·8	31·4
H	7·0	0·6	1·0	1·1	·6
N	44·8	57·6	57·2	56·3	56·8
Volumes	100·	100·	100·	100·	100·

The gases at 12·40, it will be remarked, are conspicuous for the quantity of CO_2 they contain; at the same time, in all the experiments undertaken, such an extreme case as this did not occur above three times; and here, looking at the large volume of H present, the disturbance is probably due to the admission of water near the tuyeres.

In a paper * read before the Iron Institute, I announced it as a fact, that a great number of trials justified the conclusion that, after a certain capacity of furnace was reached, no further cooling of the escaping gas took place. A curve was laid down, showing

* Transactions, 1869.

the rate at which I conceived this reduction in temperature was effected, in furnaces of different dimensions, and practically proving that 12,000 feet sufficed to rob the ascending gases of all the heat the materials were capable of receiving from this source.

This opinion, it would appear, is not universally accepted, for to the last number of the JOURNAL of the Iron and Steel Institute, Mr. William Crossley contributes a paper in which he summarily* denies the facts as I have given them, and then condemns the reasons which I adduce in explanation of phenomena whose existence he denies.

Of the facts themselves I have no doubt, and the cause of this constancy in temperature, after a certain dimension is reached, I conceive to be as stated in the language quoted by Mr. Crossley, viz. :—"A blast furnace consists practically of two fires, one at the higher, and one at the lower part of the furnace." That at the upper part derives its heat from the oxidation of the carbonic oxide by the oxide of iron, and the heat thus generated is, in part, swept out of the furnace by the current of gas.

Mr. Crossley is convinced this view cannot possibly be maintained; he regards it "as an exceedingly unsatisfactory way of getting out of a difficulty, and to make it worthy of being considered any explanation at all, it would be requisite for the process of reduction to be a heating instead of a cooling process."

In this last enunciation of opinion we agree; but he is perhaps a little rash, in the admitted absence of all experimental observation of his own, when he asserts, with the same confidence as that "night follows day" that "there are no experiments which prove satisfactorily that three equivalents of CO give out more heat than is given out when three equivalents of O combine with two equivalents of iron to form peroxide of iron, and therefore, more than will be absorbed when peroxide of iron is decomposed."

In Section XXIX. are quoted the labours of very high authorities, viz., those of Dulong and of Andrews, in connection with the investigation of the physical laws which accompany this chemical change. I have shown that the margin of heat production is not a large one, but it will be seen that their labours are in direct contradiction to the opinions of Mr. Crossley.

* Recent Investigations on the Chemistry of the Blast Furnace—*Journal of the Iron and Steel Institute*, February, 1871.

Each ton of pig iron may be regarded as containing 18·6 cwts. of Fe, and according to the last-named experimentalist 1,582 heat units are evolved when one of iron passes into the state of Fe_3O_4, so that (18·6 × 1,582) 29,425 cwt. units represent the amount of absorption which takes place in the reduction of this quantity of Fe from the state of magnetic oxide. To bring 18·6 of Fe from a state of peroxidation to the condition of metal 5·98 of C in the form of CO is required, and as each unit of this carbon emits 5,600 heat units by its conversion into CO_2, we have at our disposal 33,488 units of heat. Mr. Crossley may urge that we have no right to assume that the gasification of the larger quantity of O in Fe_2O_3 absorbs no more heat than the lesser weight in Fe_3O_4. In the appropriation of heat given in section XXIX., this source of discrepancy is alluded to, and admitting that the extra quantity of O, on taking the gaseous form, absorbs a rateable quantity of heat, we shall have to deal with 1,780 units, instead of 1,582; or for the 18·6 cwts. of iron to be reduced we shall have to provide 33,108 units.

Even here it will be observed there is a balance, but a very small one, viz., (33,488—33,108) 380 cwt. heat units. But I have shown in large furnaces that there is a greater quantity of C leaving the furnace as CO_2 than that necessary for reducing the Fe_2O_3, and that this excess is supposed to be due to the dissociation of CO to the extent of that quantity of C which finds its way into the pig iron. This action, entirely overlooked by Mr. Crossley, I have shown in Section XI. to be by far the most active at the temperatures first encountered by the ironstone on its introduction into the furnace.

From this cause we have a further heat development, stated in Section XIII. to be equal to 3,200 units per unit of carbon deposited, and assuming the ton of iron to take up ·6 cwt. of C, we have ·6 × 3,200 = 1,920. This, added to the 33,488 units evolved by the 5·98 C passing from the state of CO to CO_2, gives a total of 35,408 units, or 2,300 units above the larger of the two quantities I have deemed it possible to be needed.

It would appear, if the figures of heat absorption formerly given are to be relied on, that the action of the blast furnace itself may be called upon to afford proof of an elevation of temperature taking place in its upper zone.

The interior of a furnace may be separated into two great divisions, viz., that where the chief portion of the deoxidation and carbon impregnation takes place, and that where preparation for fusion commences and where fusion itself is completed.

So far as the lower zone is concerned, the heat development, according to the views expressed in Section XXVIII., may be regarded as equivalent to the carbon in the coke burnt to CO, *minus* a quantity equal to that entering the furnace as CO_2, carrying off its own weight by the action $CO_2 + C = 2\,CO$.

With a consumption of 22·32 cwts. of coke the actual amount of C burnt to CO in the hearth was considered to be 18·76, which is really subject to a further diminution of ·06 cwts. by the CO_2 produced by reduction of ore and carbon impregnation being reduced to CO and carrying off an equal weight of C.

The actual amount of C burnt to CO in hearth is therefore	18·70 × 2,400 =	44,880	
Brought in by the blast		11,919	
			56,799
Fusion of iron	6,600		
Decomposition of P_2O_5 SO_3 and SiO_2...	4,174		
Heat to tuyere water	1,818		
Transmission through walls chiefly occurring in the lower part of furnace ...	3,658		
Expansion of blast, &c., &c.	3,743		
		19,993	
Variable amounts of absorption.			
Fusion of slag	16,720		
Decomposition of H_2O in blast ...	2,720		
Expulsion CO_2 of $CaCO_3$	5,054		
Decomposition do.	5,248		
Evaporation of H_2O of coke	312		
		30,054	
			50,047
Surplus to commence reduction...			6,752

This mode of dealing with the question supposes the whole of the carbon introduced into the furnace to have assumed the form of CO, and it now enters upon the duties of reduction and carbon deposition, by which, according to the instance which has furnished the data just enumerated, 6·52 cwts. of the carbon contained in this

gas is converted into and escapes as CO_2, generating by the change,

	Units.
6·52 × 5,600 ... ... =	36,512
which added to the balance from the former account, viz.:—	6,752
affords for commencing the remainder of the process	43,264
These are disposed of as follows:—	
Deoxidation of ore	33,108
Deposition of the carbon	1,440
Sensible heat in gases	8,860
	43,408*

The essential feature in this statement is to be found in the circumstance that whereas only 6,752 heat units remain over for commencing the conversion of CO into CO_2, 8,860 leave the furnace after the termination of this second combustion, and where, it may be asked, arises this increase in the quantity of heat, if it is not a surplus after satisfying the requirements of this part of the process.

It may be well to remark that whether a line exists in the furnace or not, below which no reduction or chemical change takes place, does not in reality affect the argument, which, in point of fact, assumes that there are two classes of effects produced, viz., fusion, and decomposition of CO_2 in the limestone, as distinguished from the action of CO on an iron oxide. Whether these occur in distinct portions of the furnace, or a portion of each in the region considered as belonging to the other, is immaterial.

The reasons adduced for regarding some loss of heat in the escaping gases as inevitable, are doubtless more or less theoretical in their character. The waste from this cause is not a very serious one, being, as will be shown, under 10 per cent. of the fuel used, but still it is one a careful smelter would willingly avoid, were it in his power, and hence I have been at some pains in endeavouring to arrive at a sound opinion on the subject.

If it can be proved that there is a fallacy involved in the views just set forth, there is no reason why each addition to the furnace should not rob the ascending gases of some portion of that heat which escaped previously to such addition, and thus prove a source of economy in the consumption of coke. In the absence of direct experiment it

*The small difference, 144 units, is due to the deduction of ·06 cwt. C to C^O (·06 × 2,400=144).

would be difficult to lay down a curve exhibiting the extent of the cooling influence effected under such a condition of things by each increase to the capacity of the furnace. That it would alter considerably in its flexure is unquestionable, a much smaller amount of heat being intercepted by a given space as the difference between the temperature of the incoming materials and out-going gases becomes lessened.

No doubt the value of the figures just made use of is dependent upon the general correctness of the whole statement of production and appropriation of heat. If, for example, it could be demonstrated that instead of 8,860 heat units per ton of iron leaving the furnace in the gases, only 6,752 so escaped, the argument made use of would fall to the ground.

This circumstance, and the laboratory having, as has been stated, failed to afford the desired information, as to heat development, I had recourse to an experiment upon a much larger scale, which was continued for seven hours in the following manner.

Exp. 523. At a time when the charge of materials at the Wear furnace consisted of,

Coke 6·3 cwts., limestone 3·25 cwts., ironstone 12·5 cwts.,

I endeavoured to ascertain the temperature of the escaping gases. This was done by one of Siemens' water pyrometers, but as I had reason to suspect its accuracy, I judged of the actual heat by,

1st.—The insertion of a mercurial thermometer among the escaping gases.

2nd.—The fusion of different metals in a somewhat hotter portion of the gas-pipe than where the thermometer was placed.

3rd.—By the rapidity with which water boiled when thrown on to the iron pipe leading the gases away.

At the commencement of the observations, the mercury rose to 305°C. (581°F.) so rapidly that it had to be removed in a couple of minutes after its immersion; lead melted immediately, and water was evaporated with violent ebullition. I regarded, under these circumstances, that the temperature of the gases was close on that of melting zinc (417°C. or 782°F.)

The ironstone was now withdrawn, and its place supplied during 3½ hours by a mixture of a perfectly neutral character, so far as heat development was concerned. This consisted of 9 cwts. of blast

furnace slag, with 3½ cwts. of flints added, to assist in fusing the limestone, which was continued as before.

The following trials were made to compare the nature of ironstone with flints and slag for intercepting heat.

Exp. 524. *Specific gravity.*—A full charge of the ironstone, coke, and limestone occupied 55 cubic feet, while one, where flint and slag took the place of the ironstone, measured 52 cubic feet. In point of space occupied, and, therefore, of surface exposed, they may be considered as nearly identical.

Exp. 525. *Specific heat.*—The mean of four trials gave for the specific heat between 15° and 100°C—

Calcined Ironstone	·206
Flints	·200
Slag	·201

Here, again, the difference is so small as to render it unnecessary to make any correction in respect to this item.

In forty minutes after commencing to put on the slag and flints, lead ceased to melt; water no longer boiled on being thrown on to the place where, previously, it underwent violent ebullition; and the thermometer, during half an hour, never rose above 293°C. (560°F.)

During the three and a half hours, 31·15 tons of materials had been introduced into the furnace; the slag and flints were then withdrawn, and ironstone charged in their place, the thermometer standing at 240°C. (464°F.)

For an hour the thermometer never rose much above 260°C. (500°F.), the average of twelve observations being 245°C. (473°F.); lead never melted, and water, when thrown on the same place as formerly, evaporated slowly away.

During this period the ironstone acted precisely as a neutral substance—it absorbed heat, evolving none—because chemical action, for want of the Fe_2O_3 having the necessary temperature, had not set in.

During the next forty minutes the thermometer rose steadily, at the end of which it indicated 305°C. (581°F.), and water simmered slightly on the escape pipe.

In ten minutes more I was compelled to remove the thermometer, and water began to boil slightly.

After the lapse of another half-hour, lead melted and water

boiled. The observations were continued in all for three and a half hours after resuming the use of ironstone, during which 34·15 tons of materials entered the furnace, and lead, after once fusing, continued in the melted state for the remainder of the trial.

This experiment would thus point to the correctness of the previous inferences, viz., that the deoxidation of ironstone and carbon impregnation by CO, are distinct sources of heat evolution.

I trust I have now shown good cause for concluding that, after a blast furnace has reached a certain height, the gases leaving the throat will exhibit a constancy of temperature. *A priori*, this is not an extravagant supposition, for so far as the oxidation of the carbon itself is concerned, about 40 per cent. of the entire heat developed in a furnace of 11,000 to 12,000 cubic feet, is that produced by the acquisition of the second equivalent of oxygen; in other words, by the conversion of CO into CO_2. For all practical purposes, this may be considered to be effected almost exclusively in the first twenty feet of depth through which the materials pass after charging. Now it is clear, if circumstances rendered such a change desirable, the addition of twenty feet to the lower extremity of the furnace and a corresponding lowering of the tuyeres would depress the zone of fusion in like manner; why, then, should there be anything extraordinary in combustion (CO into CO_2) following the source of oxygen, which in our case is oxide of iron, by an addition to the top of a blast furnace? If the area in which this oxidation of carbonic oxide is elevated, with each addition to the height there will always exist above it the same relative quantity of material through which the heated gases will have to pass, and consequently the extent of cooling power will always remain unchanged.

At the same time it is obvious (neglecting the small amount of loss by transmission through the walls,) in the case of a furnace, charged with materials of a neutral character in a heat-producing point of view, that whatever addition is made to its capacity, there are but two modes of exit for the heat, which might thus be intercepted by an increase in the amount of cooler substance which the hot gases were made to traverse. These two modes are an increase in the temperature of the fused matters which leave the hearth, and an augmentation of temperature of the volatile constituents which are emitted at the throat. In one or both these the intercepted heat should manifest itself.

There is, I imagine, no doubt whatever that an increase of temperature in the hearth of a furnace is susceptible of beneficial application, *i.e.*, of the final fusion of a larger quantity of iron-making material, or, as will be hereafter explained, of a "richer" quality of product. The present argument is, that after a certain size of furnace is reached, any addition to its capacity does not add to the temperature of the hearth, because the heat never reaches the lower region. Further, it will be shown in the succeeding chapter that, if the higher zones have their temperature elevated beyond a certain point, either this addition makes its appearance in the sensible heat of the escaping gases, or it expends itself in producing chemical action having a distinctly cooling tendency; and in either case no advantage is derived in the practical results obtained.

If the process of reduction and carbon impregnation was of a refrigeratory, or of a neutral character, a cooling of the escaping gases would be occasioned by an increase to the dimensions of a furnace, whether this were obtained by adding to its height or width, provided the addition to the capacity were not followed by a corresponding augmentation in the amount of work done—the cooling itself being a consequence of prolonged contact between the gases themselves and the cold materials.

The simplest mode of comparing the duration of this period of contact, is by considering the weight of materials descending through the furnace, and the volume of gases ascending in a given time. For this purpose four furnaces are taken, of 6,000, 12,000, 16,000, and 26,000 cubic feet respectively, and their performances are based upon the actual results usually obtained at furnaces having approximately these dimensions. To avoid large numbers, the weights and volumes are estimated per minute of time.

Furnace of cubic feet	6000	12000	16000	26000
Height of furnace by feet	48	80	80	80
Make per week ... ... in tons ...	220 ...	260 ...	350 ...	400
Consumption of materials, per ton of iron :—				
Coke ... ... in cwts. ...	29· ...	22·5 ...	22·5 ...	22·5
Calcined ironstone	49· ...	49· ...	49· ...	49·
Limestone	16· ...	12·5 ...	12·5 ...	12·5
	94· ...	84· ...	84· ...	84·0

Approximate weight of substances, when ready for fusion, *i.e.*, after reduction of $Fe_2 O_3$, and expulsion of CO_2 from $Ca CO_3$:—

Coke and carbon, per ton of iron, in cwts.	27·	...	21·	...	21·	...	21·
Ironstone	41·	...	41·	...	41·	...	41·
Lime	9·	...	7·	...	7·	...	7·
	77·	...	69·	...	69·	...	69·

From these figures the following factors have been obtained :—

Furnace.	Make of Iron Cwts. per minute	Cwts. Materials descending per Minute.	Cubic mêtres of Gases ascending per Minute.
6,000 cubic ft.	... ·436	... 1·863	... 138
12,000 „	... ·516	... 1·973	... 132
16,000 „	... ·694	... 2·654	... 178
26,000 „	... ·793	... 3·033	... 203

The second column is calculated upon the mean weight the materials possess before and after the ore and limestone have suffered any change by the action of the furnace, and in like manner the third column represents the mean volume of gases (at 0C 760 m.m.) before and after they have absorbed oxygen and carbon from $Fe_2 O_3$ and $Ca CO_3$.

These two sets of numbers disregard the differences between the total cubic contents of each furnace. For this a correction must be made, and taking each 1,000 cubic feet of each furnace as the standard of comparison, we get for each of the furnaces :—

Furnace.	Average Cwts. of Materials descending, and Cubic Mêtres of Gas (0C 760 m.m.) ascending per each 1,000 Cubic Feet of space per minute.	
C. ft., 6,000 ...	Cwts. of materials, ·310 ...	C. mêtres of gas, 23·
„ 12,000 ...	do. ·164 ...	do. 11·
„ 16,000 ...	do. ·166 ...	do. 11·1
„ 26,000 ...	do. ·116 ...	do. 7·8

To some extent the above is a rough mode of instituting a comparison. As between the 6,000 feet furnace and the others some allowance ought, in strictness, to be made for any difference in specific heats in mixtures not consisting of precisely the same proportions of materials. Our information upon the specific heats of substances at very high temperatures, however, is too imperfect to permit this being accurately done. Nor is it of much importance, because observers are pretty well agreed that between a 6,000 feet furnace, and one of 12,000 cubic feet, there is a certain and very marked reduction in the temperature of the escaping gases, amount-

ing to something like 120°C. (248°F.) This is the result of 23 cubic metres of gas in a certain state of expansion by heat, retarded by some unknown amount of friction in rushing through the interstices, meeting in every 1,000 feet of the furnace ·31 cwts. of materials coming down, and compared with 11 cubic mêtres of gas, of which the expansion and friction are also unknown, meeting only ·164 cwts. per minute per 1,000 cubic feet of space.*

No such great disturbing influences, however, accompany the comparison between the furnace of 12,000 and that of 26,000 cubic feet. The proportions of materials are the same, the height of the columns is in both cases 80 feet, the temperature of the hearths must be identical, and I shall show immediately that the heat of the escaping gases presents no appreciable difference. In the larger furnace, however, we have the materials and gases very much longer time in contact without the latter parting with more of their sensible heat. This appears to me an unanswerable argument in favour of the view I have adopted as explanatory of constant temperature in the escaping gases.

This constancy, however, having been called into question, I have made it the subject of careful experiment, which I have been able to do in a much more complete way than formerly, by means of Mr. Siemens' electric pyrometer upon a furnace of 25,500 cubic feet. A reading was taken every ten minutes for seven hours, on two different days.

The charge of materials consisted of

Coke	37·8 cwts.
Mine	85·5 „
Limestone	18·75 „

During both days, thirteen such charges were introduced during the period of observation—the furnace running a mixture of No. 3 and 4 iron.

The average temperature of the escaping gases was—

Exp. 526.	For the first day	363°C. (685°F.)
	second day	366°C. (691°F.)

* In this mode of stating the case, no notice is taken of minor disturbance by differences in the nature of the chemical action in the upper region of a furnace of 6,000 cubic feet as compared to one of 12,000 cubic feet.

The average temperature of the blast, ascertained by twelve readings, was, for the first day ... ... 447°C. (836°F.)
second day ... ... 455°C. (851°F.)*

Now, it is worthy of especial attention, that I have never, upon any occasion, found the gases from the 12,000 feet furnace escaping at a higher average temperature than those just named.

Sufficient, perhaps, has been said on this subject, but as I am in possession of data connected with still higher furnaces than those at the Clarence Works, it may be well to mention, generally, the results exhibited by their workings, without going closely into the actual figures.

By the kindness of my friend, Mr. Williams, a long series was furnished of observations of the temperatures of the escaping gases of the Eston furnaces.

These have a height of 95 feet—15 feet more than those which have just afforded the data embodied in the previous remarks. They are of two sizes, one containing 15,000 cubic feet, and the other 26,000 cubic feet. They are supplied with material precisely of the same character, and are worked precisely in the same way as the Clarence furnaces. Their production, at the period of trial, was 320 tons and 360 tons per week respectively, the gases would, therefore, have a somewhat longer opportunity of communicating their sensible heat to the descending materials, than happened at the Clarence Works.

Notwithstanding all these circumstances, I may summarise the results as follows:—

They consume no less coke, per ton of iron, than do the Clarence furnaces; the gases are fully as hot as those at this work; and, lastly, the gases from one Eston furnace of 26,000 cubic feet are no cooler than those from another of little more than half its size, and the consumption of coke per ton of iron was the same in both.

Again, at Ferryhill, the furnaces are of two kinds; one, 80 feet high, and containing 16,000, the other, 103½ feet in height, and containing 33,000 cubic feet. At the period of my visit, the weekly

* I would remark, in reference to this pyrometer of Mr. Siemens, that there has been one in use at the Clarence works for upwards of two months. To check its indications, a seconds pendulum is hung near the tuyeres, and as nearly as can be the time is ascertained required to melt a rod of zinc ⅛ of an inch in diameter placed in the blast pipe. During this period there seems no change, and as far as I can judge, the information it affords may be relied on.

make of the former was at the rate of 340 tons, and had the production of the other been in proportion to this, it ought to have run 700 tons. The make of the latter, however, was only 540 tons per week. In spite of the better opportunity possessed by the larger furnace of robbing the escaping gases of their heat, the temperatures did not differ by above 6°C. (11°F.)*

To ascertain in a rough way the comparative rate of increase, as we descend, in the temperature of two furnaces of different heights, I had holes drilled in their sides, so as to view the condition of their contents. The following affords an idea of the state of the two:—

Distance from Top.	48 ft. Furnace. Exit gases Temperature :—452°C. (846°F.)	80 ft. Furnace. 332°C. (627°F.)
4·25 ft.	Black ...	Black.
9·75	Dull red heat ...	do.
15·50	Bright red heat ...	Dull red heat.
21·25	Very bright red ...	Bright red.
26·75	... ...	Very bright red.

Thus, within a few feet, reckoning from the top, the temperature becomes apparently the same in each case, viz., at 21·25 feet in the 48 feet, and 26·75 feet in the 80 feet furnace.

For the reasons described, there is undoubtedly considerable loss in smelting freshly calcined Cleveland ore in a furnace 48 feet in height, for the cwt. heat units carried off in the escaping gases were ascertained to amount to 19,000 or 20,000; whereas, in one of 80 feet, the loss was reduced to 11,000 to 12,000 units.

Some doubt appears to be entertained as to the representative in coke of this quantity of heat. Mr. Charles Cochrane, at a meeting of the Iron Institute, mentioned my dividing "an apparently correct numerator by a fictitious denominator," and thus falsifying the result; and Mr. Crossley, in the paper already mentioned, in effect repeats this statement. These gentlemen practically contend that, inasmuch as the coke is burnt in the hearth to CO, we have to divide the heat units saved by those evolved by the conversion of C into its first stage of oxidation, and, further, that no account should be taken of the heat brought in by the blast.

* At both, the gases were much cooler than at furnaces using ironstone hot from the kilns. At Ferryhill, the ironstone is calcined at the mines 40 miles off.

Surely, it cannot be denied that if the whole of the carbon were burnt in the hearth to CO_2, the denominator should be that representing C to CO_2; and it seems equally clear that if part of the C were converted into CO, and part into CO_2, the value of C as a heating agent would be raised accordingly. Whether this second and partial oxidation takes place in one part or the other of the furnace, seems to me immaterial. Again, why should the heat contributed by the air be lost sight of? The whole three, *i.e.*, C to CO, CO to CO_2, and the blast, go to build up the sum of the total number of heat units evolved in the furnace; and it would, therefore, be as reasonable to exclude the part taken by one of these sources of heat in the fusion of the iron as to deny it a place in the escaping gases. If C to CO is the true "denominator" in one case, it must be so in all, and this would restore the relation as to heat consumption among every step of the process, but it certainly would not express the actual number of heat units absorbed.

In Section XXVIII., I gave 104,012 cwt. units produced by 28·92 cwts. of coke. I, therefore, say, 104,012 ÷ 28·92 = 3,596 units per cwts. of coke. With a consumption of 22·32 cwts. of coke 93,455 units were the product, and 93,455 ÷ 22·32 = 4,187 units. To ascertain really the exact loss arising from the heat carried off in the gases, an allowance ought to be made for that brought in by the materials themselves. This is a quantity which it is almost impossible to estimate exactly; but, in a furnace of 12,000 cubic feet, after making an allowance in the manner already described, I have assumed 8,860 units of heat, generated by the combustion of fuel, as lost from this cause, and 8,860 ÷ 4,187 is equal to 2·11 cwts. of coke.

SECTION XXXIII.—ON THE CAPACITY REQUIRED BY THE BLAST FURNACE TO ENABLE THE CO TO BECOME SATURATED WITH OXYGEN.

In many instances of chemical action, combination is so rapid as to be considered instantaneous. Free oxygen and carbonic oxide mixed, explode on the application of heat, and if the two are in suitable proportions, the CO and O entirely disappear, and carbonic acid is the immediate result. There are, on the other hand, many other cases in which time is an important element, and any

sacrifice in respect thereof must be met by some mode of compensation by which the defect in question may find a remedy.

After what has been said in previous sections of this work on the antagonism which arises between CO in effecting the reduction of an iron oxide, and the CO_2 generated by the operation itself, the saturation of the reducing gas in smelting iron is the reverse of rapid, particularly in the case of certain ores, which we have seen yield their oxygen much less readily than some others. It is, under these circumstances, quite intelligible that a gas, rushing with immense velocity through the materials which fill the furnace, may not have sufficient opportunity, before reaching the top, of taking up that full dose of oxygen which experiment and experience demonstrate them to be capable of holding. To compensate for this want of time to enable the gases to effect their object, the smelter is compelled to use a gas of a more powerful reducing order than he need do could he give it more time to do its work. The reducing agent thus speedily effects the required duty, by the operation being confined to that period where its power of deoxidation has not become blunted by any considerable previous amount of oxygen absorption. To obtain increased activity in the reducing power of the current of gas streaming up the furnace, there is but one alternative under the supposed conditions. The oxygen in the ore per ton of iron produced is a constant quantity, and the only way to neutralize its effect on the gases themselves is to dilute it with more carbon—in short, to use more fuel.

Let us, in the first place, consider the extent of unexpended chemical force which is permitted to be wasted by the premature escape of carbonic oxide, *i.e.*, before it has taken up all the oxygen it is capable of absorbing, and, as an example, the case of one of the older furnaces of 6,000 cubic feet, smelting Cleveland stone, will be examined.

The CO generated in the hearth of such a furnace may be regarded as reaching the outlet pipe, when such a portion of it was converted into CO_2 that the composition of the escaping gases by weight was—

CO_2	... ...	11·75
CO	... ...	30·58
N	... ...	57·67
		—— 100*

* To avoid complication the hydrogen and hydro-carbons are omitted.

In this mixture, 100 vols of CO are associated with something under 25 vols. of CO_2. But it has been demonstrated, that until 100 vols. of CO were accompanied by nearly double this quantity of CO_2 it possessed considerable reducing powers on Cleveland ore at the temperature of melting zinc. Turning to the gases themselves, as they leave such a furnace as the one under consideration, Exp. 112 *et seq.* show the activity they possess in reducing this quality of stone, for in six hours above half the oxygen contained in Cleveland ore was removed, on its being placed in the escape pipe of a furnace of 6,000 cubic feet.

It is, however, not enough that we should have a richer reducing gas to make amends for the want of time during which it is in contact with the oxide of iron to be operated upon; we must, in addition to this, have it very much hotter, which, as the experiments in Section VIII. proved, greatly accelerates the action of deoxidation.

From a statement in Section XXXII., it was shown that, after the other work of the furnace was satisfied in respect to heat requirement, there was a balance remaining for commencing the operation of deoxidation, amounting to 6,752 cwt. heat units. The following is a statement of the work of a 6,000 ft. furnace when it was consuming 28·92 cwt. of coke, framed upon the same basis as that just quoted :—

The carbon in 28·92 cwts. of coke was taken at			26·36
The limestone contained 1·92 as CO_2, which would carry off by action $CO_2+C=2\,CO$		1·92	
There would be generated by reduction and carbon deposition as CO_2 of C		6·58	
There was really in gases...		5·47	
Difference (also carrying off C) ...		1·11	
Total C in CO_2, carrying off equal weight of C			3·03
Actual C burnt in hearth...			23·33
23·33 C to CO = 23·33 × 2,400		= 55,992	units.
Blast estimated to contain		14,724	„
		70,716	„

Brought forward			70,716 unt.
Absorption for fusion of iron, &c., same as in furnace of 11,500 cubic feet, Section XXXII		19,993	
Variable amounts of absorption—			
Slag, as per table in Section XXVIII.	17,710		
Decomposition of H_2O of blast ...	3,740		
Expulsion of CO_2 in $Ca\,CO_3$ ...	5,920		
Decomposition do. ...	6,144		
Evaporation of H_2O in coke ...	399		
		33,913	
			53,906
Surplus to commence reduction			16,810

In the statement in Section XXXI. alluded to, 6,752 units entered the zone of reduction and carbon deposition, and then left it 8,860; showing an increase of 2,108. In the instance just quoted, reduction and carbon deposition were commenced with 16,810 units, while there was present in the gases 16,409, which is a decrease of 401 units.

The above statement has been compiled to explain what may appear at first sight to be contradictory to the opinion previously set forth, viz., that the heat which remained over from the work of the lower part of the furnace experienced a marked increase in quantity after providing for the requirements of the upper.

It will be found this arises from the difference in the temperature of the two furnaces now being compared with each other. In the former, the heat of the upper portion of the furnace was such as to permit almost all the CO_2 once generated by deoxidation of Fe_2O_3 and carbon deposition to escape as such; in the latter 1·11 cwt. less C per ton of iron than that due to the action of CO on the ore is found in the escaping gases.

It is clear that the gases themselves, before commencing the operation of reduction in the lesser furnace, possess a higher temperature than they do in the larger, for in the former, about 154 cwts of gas contain 16,810 units, whereas in the other, 124 of gas only carry 6,752, both calculated before the CO commences to act on the iron oxide. Now, $\frac{16{,}810 \text{ units}}{154 \text{ cwts} \times \cdot 24 \text{ SH}}$ gives a temperature of 454°C. (849°F.), against which we have $\frac{6{,}752 \text{ units}}{124 \text{ cwts.} \times \cdot 24 \text{ SH}}$ equal to 227°C. (440°F.)*

* The weight of gases taken above is simply that of the blast, and carbon in the coke, which is near enough for the demonstration in question.

It must, of course, not be understood that these two numbers do more than express the temperature produced by the action in question, irrespective of any accumulation by interception of heat previously taken up by the materials from the gases. The extent to which this takes place will be examined in a future section.

The immediate cause of this disappearance of heat is, as has been already stated, the higher temperature of the gases entering what we are considering the zone of reduction. It will be remembered in Section VII., the manner was fully explained in which CO_2 was resolved into CO as the temperature rose, giving rise to an increased activity of the tendency E*, described in Section XV. causing a heat absorption by CO_2, escaping as CO.

Put in other words, this waste of calorific power is the result of a compromise rendered necessary by the want of time for the gases to absorb their full quantity of oxygen from the iron oxide. High temperature in one part of the process may have become necessary to supplement the power of the carbonic oxide, which is detrimental in another by setting up a condition of things where the CO_2, produced by the reduction of the ore and carbon deposition, is brought back to the state of CO, a change which is accompanied by a notable loss of heat.†

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* Tendency—E. Action of CO_2 set free in other reactions upon carbon, metallic iron, and lower oxide of iron.

†Following out the heat statement of the upper zone of a 6,000 feet furnace, we have:—

Total heat evolved in hearth, as given		70,716 units
Heat absorption of lower zone do.	53,906	
Less a difference between columns A and B, in table of Constant Requirements, arising in absorption account...	851	
		53,055
Surplus to commence reduction ...		17,661
Heat evolved in upper zone—		
5·47 C as CO to CO_2, 5·47 × 5,600 = ...	30,632	
1·11 C of coke burnt to CO in upper zone by CO_2, resulting from carbon impregnation and reduction, $CO_2 + C = 2\,CO$ 1·11 × 2,400 = ...	2,664	
		33,296
Affords for remainder of process ...		50,957
These are disposed of, as follows:		
Deoxidation of ore	31,108	
Carbon impregnation	1,440	
Sensible heat in gases	16,409	
		50,957

Thus, 17,661 units, along with nearly the whole of 2,664, or together, 20,325, appear as only 16,409 in the gases, showing a diminution of 3,916 units. This is almost entirely accounted for by the change of the CO_2 to CO, for 1·11 C × 3,200 = 3,552, the difference between this number and 3,916 no doubt being experimental error.

In comparing the work performed by a furnace, where the time of exposure is short of what is required, with that of another in which this defective mode of procedure is absent, we can without much difficulty ascertain how the loss arises.

For this purpose, the examples formerly given in Section XXVIII. of a 6,000 feet furnace consuming 28·92 cwts. of coke, and one of 12,000 cubic feet using 22·32 cwts. of coke per ton of iron will be taken.

Coke consumed in the furnace, 6,000 cubic feet	...	28·92
do. do. 12,000 „	...	22·32
Difference	...	6·60

This is made up as follows—taking each cwt. of coke in the lesser furnace to evolve 3,596 units:—

For CO_2 of limestone expelled and decomposed, 6,000 feet furnace	...	12,064 units.	
Do. 12,000 „ do.	...	10,302 „	
		1,762 „	= ·49 coke.
Greater quantity of slag fused in 6,000 feet furnace	...	= 990 „	= ·27
Sensible heat in the escaping gases in 6,000 feet furnace	...	16,409 „	
Do. in 12,000 feet furnace	...	8,860 „	
Difference		7,549 „	= 2·10 coke.
Carbon wasted in smaller furnace by (CO_2+C=2 CO) in excess of larger=1·11—·06...	...	...	1·05
Balance, being coke required to confer greater reducing power on gases rendered necessary by shortness of time during which ore was exposed in smaller furnace	...	...	2·69
			6·60 coke.

The defect, then, of a furnace of inferior capacity consists in the gases passing through it so quickly that they have neither time to

communicate all the sensible heat they are capable of imparting to the descending materials, nor to absorb all the oxygen they are capable of holding,

We have just seen how the presence of greater heat, and the necessity for more carbon in the gases is productive of a great increase in the consumption of fuel.

It might be thought that this loss of fuel is susceptible of amelioration by prolonging the time of exposure of the ore to the gases, a result readily commanded by a slower driving of the furnace. This mode of remedying the defect just described was tried some years ago at the Clarence works, with results the reverse of what might have been anticipated.

During a whole month, the average make of six small furnaces at this place was 246·15 tons per week, of average quality, represented by No. 3·73, with a coke consumption of 27·5 cwts. per ton.

Without any apparent reason, when the speed of working was slackened, the effect produced at the same six furnaces, over some weeks, was as follows :—

Weekly make per Furnace.		Average Quality. Number.		Coke per Ton of iron.
219	...	3·45	...	28·98
206	...	3·20	...	31·06
186	...	3·60	...	30·34

The increase in the fuel consumed is not strictly in accordance with the change of rate in driving, which may be due to other causes, but I give the figures as an illustration of a fact taught by actual experience, viz., that a lessened make does not produce beneficial results unless the reduction is consequent upon the furnace having been driven beyond its powers.

An enquiry into the cause of this apparent anomaly is not without its use in considering the action of the blast furnace. In endeavouring to analyse the sources of the heat developed in its interior, and to apportion the appropriation, it must not be supposed that the quantity of heat evolved and absorbed per unit of iron affords any idea whatever of either the intensity of heat or of the actual quantity stored up, as it were, in the materials solid and gaseous, filling its interior. A calculation will be hereafter given of the quantity of heat evolved during the blowing-in of a furnace, and its retention by the cold materials constitutes a very large magazine,

which remains practically undisturbed to any great extent while the furnace continues in blast. Fresh heat is evolved, which in part is absorbed by the process of smelting, and in part is passed away with the gases, without greatly interfering with the actual quantity which accumulated when the furnace was first started.

The effect of this interception of heat is an extension of the area of intense heat much beyond what it otherwise would be, so that at a depth of 15·5 feet in a furnace 48 feet high, the temperature, as we have seen, is bright red, and in that of one of 80 feet, a similar heat prevails at a distance of 21·25 feet from the top. In the first-named instance this will embrace a cubic capacity of about one-fourth of the whole contents, viz., 1,500 cubic feet, and in the second about 2,600 cubic feet, or 23 per cent. of the whole. Now, in both these cases, analyses proved that nearly nine-tenths of all the oxygen contained in the minerals, viz., that in Fe_2O_3, and $CaCO_3$, was found in the gases before they reached this point, so that in the matter of deoxidation, three-fourths of the interior of a blast furnace may be regarded as almost neutral, as will be understood where the composition of the gases from the top downwards comes to be given.

I unfortunately possess no examination of the gases made during the experiments, nor have I any record of their temperature; but the explanation I would give of the want of success in saving fuel by slow driving is as follows. The incoming materials would acquire more heat, in the first instance, by virtue of their longer contact with the ascending gases, but the value of this would never reach the hearth, but would simply produce a still greater extension of the space upwards occupied by incandescent matter, so that the amount of reduction in the 48 feet furnace, just spoken of, instead of occupying 1,500 cubic feet for its accomplishment, would commence and be perfected in a lesser space, from its higher temperature. The effect of this change would be, that although the materials descended, and the gases ascended more slowly than they did with more rapid driving, yet, as deoxidation and the heat evolution attendant thereon were performed in a shorter space, practically the gases were not better cooled by the operation. Indeed, this and a possible less perfect saturation of the gases with oxygen, is the only way, it appears to me, of accounting for the fact, that instead of there being any economy, there was a positive loss, by a diminution in the amount of work done.

So far, then, it is clear the addition of 6,000 cubic feet to the original furnaces in the vicinity of Middlesbrough has been followed by an economy of 6 to 8 cwt. of coke per ton of iron, which has arisen from the three sources just named, *i.e.*:

1st. More perfect absorption of heat from the ascending gases.

2nd. Preserving CO_2 once formed by the reduction of the ore, by avoiding the action $CO_2 + C = 2\,CO$.

3rd. Enabling the reducing gas to effect reduction with a lessened quantity of CO.

In the previous section, I endeavoured to prove, that so far as any further reduction in the temperature of the escaping gases is concerned, we must be content with submitting to a loss equivalent to about 2 cwt. of coke from this cause, when smelting calcined Cleveland ironstone, and that in consequence, no addition to the dimensions of a blast furnace will be productive of any marked advantage so far as this source of waste is concerned.

Before dismissing this branch of the subject, it may be observed that the sensible heat contained in the gases must not be regarded as loss, for a very large quantity of this heat finds its way into the fire-places of the air stoves and boilers, and is productive of benefit exactly in the same fashion as heating the gases in one of Siemens' regenerative furnaces, *i.e.*, the temperature evolved by the combustion of the waste gases is raised by the exact amount of sensible heat they contain. At the same time, it must be admitted, as a mere matter of economy, it would be better to avoid the sacrifice of coke—an expensive form of fuel—in the blast furnace, even if its place had to be supplied by small coal, which, in the Cleveland district, is not much above one-fourth of the price of the former article.

With regard to the two other heads of possible economy to be obtained by the use of still larger furnaces, a moment's reflection will satisfy us that to reap any benefit from their action is equivalent to admitting the presence of a larger quantity of CO_2 in the gases than has been hitherto found to exist therein.

Suppose a furnace working, with its full complement of ironstone, so as to emit for each ton of iron produced 6·58 cwts. of C in the form of CO_2, which we have considered as the quantity representing the deoxidation of the ore, and carbon dissolved by the iron. In any case, this is the maximum quantity of CO_2, which can be

generated for each ton of metal, and the question, therefore, is, what is the minimum quantity of CO with which it must be associated before the mixture ceases to exercise a reducing action.

For an answer to this interrogatory, we must again refer to the different experiments undertaken with a view to ascertain the point beyond which CO appears unable to withdraw O from Fe_2O_3 as it exists in calcined Cleveland ironstone.

These were referred to so recently, when we were considering the extent to which heat produced by the generation of CO in the hearth could be supplanted by heat contributed by the blast, that it would be a waste of time going over the same ground at any length again. It was proved by reference to experiments given in section VIII., that somewhere between 31 and 50 vols. of CO_2 almost completely paralyzed the reducing power of 100 vols. of CO. To save time in referring to the experiments themselves, the results bearing on this question were :—

Exp.	Vols. CO_2 per 100 Vols. CO.	Temperature.	Time.	Percentage of original O removed.
104	31	Melting zinc	5 hours	1·9
106	„	do.	10½	2·9
107	„	Low red heat	5	29·3
95	50	Melting zinc	5½	·9
99	„	do.	11½	4·3
102	„	do.	6	5·8
85	100	Bright red	5½	14·8
81	125	Above melting zinc	1¾	5·25
84	220	Red heat	1½	11·70
83	400	Full red	1	15·70
82	600	Low red	½	5·80

It must be observed that the question before us is not the power of calcined Cleveland ore in unlimited quantity to change a limited amount of CO entirely into CO_2, which indeed it is capable of doing, but the point at which Fe_2O_3 and CO in fixed relations, a certain proportion of CO_2 stops the process. For example, in exps. 85 to 89, four different varieties of peroxide of iron and one of pure spongy iron were exposed at a red heat to the action of oxalic acid gas (equal vols. CO and CO_2.) The operation was continued until all further action ceased. The oxide of iron lost and the metallic iron absorbed oxygen until the composition of all were equal, and

this change was permanent. It is obvious, under these circumstances, no quantity of such a mixture of CO and CO_2 could ever tear away O from Fe_2O_3 below the point indicated in the experiments, which was almost exactly 33 per cent. of the whole quantity contained in this compound of iron and oxygen.

Neither is it a question whether at higher temperatures than those at which the gases emerge from the solid materials contained in the furnace, they can deoxidize iron ore. We have, for example, an instance of 400 vols. of CO_2 to 100 of CO, in experiment 83, abstracting 15·7 per cent. of the oxygen from calcined Cleveland ironstone at a full red heat. We would have, in this case, as in experiments 85 to 89, just described, to encounter the same difficulty, mentioned when equal volumes of the two gases were employed, differing only in degree, viz., a point of reduction below which a mixture containing this proportion of CO_2 is powerless.

But supposing it were considered expedient, in the hope of augmenting the reducing power of the gases, to communicate to them by some means or other a higher temperature, say, that of bright redness, or about 1,000°C. (1832°F.), by which change they could, instead of being inert, when 100 vols. of CO carries with it 50 vols. of CO_2 at melting zinc, go on absorbing O until the ore lost 33 per cent. of its O, and the gases were composed of CO and CO_2 in equal volumes.

The quantity of heat contained in 140 cwt.* of gases at this temperature would be $140 \times 1{,}000° \times \cdot 24$ SH = 33,600 cwt. heat units, which is equal to nearly 4¼ cwt. of coke burnt to CO_2, and to 14 cwt. if only burnt to CO.

Were any advantage to accrue from such a mode of conducting the operation, the heat in the escaping gases will be somewhat different from that already indicated; but inasmuch as it will be proved in a subsequent section that there are other phenomena connected with the action of the blast furnace, which would effectually annihilate any gain from the plan of procedure now suggested it is useless to pursue the enquiry any further.

Instead of this unprofitable labour, let us rather consider whether any additions which have been made to the dimensions now under examination have been attended with any increase in the quantity

* 140 cwt. is roughly the weight of gas per ton of iron from a furnace of 12,000 cubic feet, smelting Cleveland stone.

of CO_2 to be found in the escaping gases. In other words, does a furnace of 12,000 cubic feet make its iron with as little coke as one of twice its capacity?

Now, there is nothing easier than to persuade oneself that this or the other furnace is doing better or worse than some other with which it is compared. In such an enquiry, it is absolutely indispensable that all disturbing causes should be eliminated—and every instance brought down to one common level in respect to the coke, ironstone, and limestone consumed, temperature of the blast, and every other circumstance connected with its working. Of course, it is mere deception to take a furnace of, say, 20,000 cubic feet and compare it to one of 12,000, if the latter were not in its highest state of efficiency from the use of indifferent coke, poor ironstone, or badly heated air, and equally fallacious would it be to pretend that a furnace of 20,000 cubic feet with its air heated to 1,400°F. does much better than the same furnace with the blast at 1,000°F., if it can be shown from some cause or another that when the blast was at the lower temperature the coke consumption was abnormally high.

It is extremely difficult, from such a visit as a stranger can pay to any work, to appreciate thoroughly all the conditions which, during his absence, have conduced to a favourable state of things or the reverse. Indeed, a furnace with apparently, and indeed really, all the visible conditions as to materials and blast identical with its neighbour may be doing badly from some impediment inside, which, either by bringing down extra matter to fuse, or by creating channels through the materials, permits the gases to rush up and out of the furnace before they have performed that amount of duty experience shows they are capable of exercising.

To clear up the object in view, the proper way is to discard all cases of working below that recognised standard at which for weeks and months furnaces of certain dimensions are capable of working, and deal only with them when doing fair duty.

Now, in support of the statement that CO_2 never exceeds certain proportions in gases emitted by furnaces smelting Cleveland stone, all I can say is, that from those working at the best, 40 to 45 vols. of CO_2 per 100 vols. CO has never been exceeded.

In illustration of this, the following instances are given.

Exp. 527. Ferryhill furnace, 80 feet high, containing 16,000

cubic feet, smelting Cleveland top seam, average of eight analyses of samples, taken over 2½ hours.

CO_2	...	9·6 vols.	100 vols. CO=33·6 CO_2
CO	...	28·5 „	
H	...	1·6 „	
N	...	60·3 „	
		100·0 „	

Exp. 528. Ferryhill furnace, 103½ feet high, containing 33,300 cubic feet; average of eight analyses of samples taken over three hours:—

CO_2	...	10·1 vols.	100 vols. CO=34·9 CO_2
CO	...	28·9 „	
H	...	1·5 „	
N	...	59·5 „	
		100·0 „	

In neither of these does the CO_2 come up to that found in other cases, and the difference observable in favour of the larger furnace was, so far as I could judge, entirely attributable to the better heated blast supplied to it, as compared with the other.

Exp. 529. Ormesby, 76 feet high, 20,640 feet capacity, blown with air at 780°C. (1,436°F.) smelting Cleveland ore: average of ten samples taken over three hours:—

CO_2	...	10·7 vols.	100 vols. CO...34·6 CO_2
CO	...	30·9 „	
H	...	1·3	
N	...	57·1	
		100·0	

Exp. 530. Consett furnace 55 feet high, 11,400 cubic feet. Smelting mixture of Cleveland low seam and hæmatite yielding 48 per cent. Blast, 454·5°C. (850°F.) Average of 5 samples over 3 hours:—

CO_2	...	9·7	100 vols. CO=31·90 CO_2
CO	...	30·4	
H	...	1·9	
N	...	58·0	
		100·0	

Exp. 531. Consett furnace, 55 feet high, 10,300* cubic feet, smelting same as above. Blast 718°C. (1324°F.) Average of 5 samples over 3 hours:—

CO_2	...	11·8	100 vols. CO = 40·00 CO_2
CO	...	29·5	
H	...	1·2	
N	...	57·5	
		100·0	

Exp. 532. Clarence 11,500 feet furnace, 80 feet high, smelting Cleveland stone. Average of 8 analyses over 4 hours:—

CO_2	...	11·75	100 vols. CO = 44·14 CO_2
CO	...	26·62	
H	...	·7	
N	...	60·93	
		100·00	

Exp. 533. Clarence, 25,500 cubic feet, 80 feet high,—smelting usual Cleveland stone; 7 samples, taken over 3¼ hours:—

CO_2	...	11·6	100 vols. CO = 40·3 vols. CO_2
CO	...	28·8	
H	...	1·2	
N	...	58·4	
		100·0	

Exp. 534. Clarence, 11,500 cubic feet furnace,—smelting Cleveland stone. Average, of 12 analyses, 4½ hours:—

CO_2	...	11·5	100 vols. CO = 39·64 vols. CO_2
CO	...	29·0	
H	...	1·6	
N	...	57·9	
		100·0	

Exp. 535. Clarence, 15,500 cubic feet furnace,—smelting Cleveland stone. Average of 10 analyses over 3 hours:—

CO_2	...	10·4	100 vols. CO = 35·4 vols. CO_2
CO	...	29·4	
H	...	1·3	
N	...	58·9	
		100·0	

* Upon the occasion of my former visit, the contents of the Consett furnaces were stated to be 9,414 cubic feet. The above dimensions are marked on a recent plan.

Now, there is nothing to justify the expectation, from these analyses, that CO_2 ever reaches 50 vols. per 100 vols. of CO; on the contrary, there is strong presumptive proof that it rarely reaches 45 of the one to 100 of the other.*

Again, experiments 127, 128, 136, 137, 138, and 139 may be quoted in support of the doctrine, that when 100 vols. of CO in the actual furnace gases are accompanied by 39 to 44 vols. CO_2, their action is of the feeblest character on calcined Cleveland ore, to which material, at the present moment, we are confining our attention.

So much for the results obtained by means of special experiments. A word or two in reference to general experience. At the Clarence Works there are furnaces of 11,500, 15,500, and 25,500 cubic feet, and all 80 feet in height. These have been in operation for two to six years, so that by this time, we ought to be able to form a tolerably correct idea of the relative value of each in point of consumption of coke. Now, the result of this experience is, that with all conditions equal, there is no perceptible difference to be detected. Were I to choose, perhaps, as a mere matter of regularity in working, I probably would give the preference to a furnace having a capacity of 15,000 to 16,000 cubic feet, but beyond these dimensions, I maintain that nothing has come under my notice to induce me to hope for any advantage, so far as saving of fuel is concerned, by any further addition to height or size.

I should scarcely venture to express myself in such confident terms, had not the views founded upon a lengthened study of the properties of the agents we have to deal with, and confirmed by practical experience, been adopted by others equally able with myself to pronounce an opinion upon this important question.

I cannot, perhaps, appeal to a higher authority than my friend Mr. Edward Williams, the very able manager of the extensive works of Messrs. Bolckow, Vaughan, & Co.:—"We have," he observes,† "close together, at the Eston furnaces, one of 15,000 feet capacity, one of 20,000 feet, and another of 27,000, all using pre-

* Of course, the proportion of ore to coke determines *a priori* the relation between CO_2 and CO in the escaping gases; but the fact of the CO_2 therein, never being quite equal to the O existing in the Fe_2O_3 in Cleveland ironstone, is accepted as the proof of a limit to its relative quantity.

† Transactions, Iron Institute, 1870.

cisely the same ironstone, with fuel from the same colliery; and, so far as we are able to judge, there is no economy in the larger furnaces." Mr. W. goes on to say—"This is quite certain, that in any case beyond 11,000 or 12,000 feet capacity, there is no saving of coke per ton of iron made."

It will be remembered, the Eston furnaces are 15 feet higher than those at Clarence, viz., 95 feet instead of 80 feet; and, further, I am able to state that their consumption of coke is as identical with that at the latter works as it is possible to imagine.

In the previous Section it was, I trust, sufficiently clearly demonstrated, that in smelting calcined Cleveland ironstone, a capacity of 12,000 feet in a furnace 80 feet in height, sufficed to prevent any avoidable waste by the presence of sensible heat in the waste gases. I hope it has been equally clearly proved that a furnace having these dimensions, when properly worked, is large enough to enable CO to become properly saturated with oxygen gas.

The question of a blast furnace having sufficient dimensions to perform its duty with the maximum state of efficiency, has been treated under two distinct heads, viz., its power to intercept heat from the ascending gases, and to have these gases as fully saturated with oxygen as the nature of the process admits. It is, nevertheless, to be remembered, that ultimately the whole question turns upon the last of these two conditions, and it is in consequence difficult to consider the first independently of the second.

In all blast furnaces the centre of greatest heat is of course near the tuyeres. The temperature of the contents gradually diminishes upwards, but extends far beyond what it otherwise would, from the materials absorbing a very large amount of heat from the gases.

In a furnace of 48 feet in height, and containing 6,000 cubic feet, the reducing zone, and therefore the upper part, when smelting Cleveland stone, cannot be said to be beyond the influence of the heat from the tuyeres, for we have seen that 16,810 units remained over after the operations proper to the lower zone had been effected. In stating that the progress of reduction and carbon deposition were attended with an actual rise in temperature, it is nevertheless true that for this all, or nearly all, the CO which is transformed by the operation into CO_2 must escape as such: thus, in the manufacture of one ton of pig iron, 6·58 cwts. of C in CO was considered as passing into the state of CO_2, affording (6·58 × 5,600) 36,848 cwt. heat

units; whereas, the extreme absorption of Fe_2O_3 reduced to 18·6 cwts. Fe was estimated to be 33,108, leaving a balance of 3,740 units.*

With this state of affairs, it was maintained that there were virtually two fires or sources of heat in the blast furnace, one at the tuyeres where C was converted into CO, and the other at the top, where CO generated CO_2.

Now, in such a furnace as that we are speaking of, viz., one of 6,000 cubic feet, only 5·47 cwts. of C escaped as CO_2 per ton of iron, affording by the change only 30,632 units; and here it might be urged, as 33,108 units are absorbed for deoxidising 18·6 cwts. of iron, there is a cooling instead of a heating process in operation.

This may be and is quite true, if the duty of the whole zone is taken into the account, but this is not the correct mode of viewing the matter. The temperature of the escaping gases from the furnace in question is a little above that of melting zinc. At first, reduction will commence below even this point, because it will be some time before the materials themselves acquire the same heat as the escaping gases.

It is highly probable that the first portions of oxygen are removed more easily than the succeeding ones, but omitting this possible advantage, there is no kind of doubt that the first steps of deoxidation and carbon impregnation, *i.e.*, those at the very top of this furnace—will be effected without any of the resulting CO_2 being resolved into CO, simply because the heat is not sufficient to permit the reaction $CO_2 + C = 2\ CO$. Indeed, looking at the actual quantity of C as CO_2 in its gases (5·47 instead of 6·58), it would appear 83 per cent. of the action belonging to the upper region is accomplished without the antagonistic process of CO_2 dissolving carbon being called into play.

It is obvious, therefore, even here, there is at the top of the furnace a heat-producing change so far as 83 per cent. of the ironstone is concerned, and, therefore, quite enough to account for the extension of the space filled with incandescent materials, when furnaces of 6,000 cubic feet were driven at "slack blast."

We must now regard 83 per cent. of the oxide of iron reduced and carburised descending through the furnace without any of the resulting CO_2 being resolved into CO. The remaining 17 per cent.,

* This balance has also to provide for the heat absorbed by carbon deposition.

however, of the ore does not part with its oxygen until it reaches such a depth as to have come within the influence of the heat emanating from the intense combustion going on in the hearth, and then reaction takes place, viz., the absorption of C by CO_2 with its attendant loss of heat.

Notwithstanding what has just been advanced, it must not be imagined that there exists a line in the upper part of the furnace, above which no CO_2 is split up into CO, and below which all CO_2 experiences this change. Every foot of depth has its atmosphere kept in a state of equilibrium by the exercise of the five tendencies mentioned in Section XV. The manner in which CO_2 disappeared as the temperature rose in presence of metallic iron, and the behaviour of $Fe_2 O_3$ and Fe in mixtures of CO and CO_2 were sufficiently explained in Sections VII. and VIII., to render it perfectly intelligible that the extent of conversion of CO_2 to C must be gradual, increasing in amount as the temperature of the space in which reduction is accomplished rises.

Now, the advantage of a large furnace may be regarded as the removal of the zone in which deoxidation and carbon deposition take place so far from the tuyeres as to place it beyond the reach of the very high temperature produced by too great proximity to the hearth, by which means the detrimental effect of the decomposition of CO_2 is avoided. Once this is done, then the furnace has reached the necessary dimensions to work with the maximum amount of CO_2 in its escaping gases, *i.e.*, with the minimum quantity of fuel.*

If these dimensions are exceeded, there is established in the furnace, so far as reduction and carbon impregnation are concerned, a region of a neutral character, perhaps not without some advantage in ensuring regularity of action, but of no value in altering the power of the gases to hold above a certain quantity of carbonic acid. I hope to be able to prove, by experiments now in progress, that the difference between a furnace of 12,000 and one of 25,000 cubic feet consists in a large expansion of this neutral space.

The very same line of reasoning which has been pursued in reference to the dimensions of a furnace is equally applicable to the temperature of the blast—the question must be ultimately decided by the quantity of oxygen the gases are able to absorb,

* With the full equivalent of CO_2 in the gases, the reduction of their temperature may be considered concurrent.

which, in the case of calcined Cleveland stone, I have supposed to be done when 140 to 145 volumes consist of 100 volumes CO, and 40 to 45 of CO_2.

Let us conceive a furnace working under these conditions as to composition of escaping gas, with its blast at 475°C. (887°F.), and where the air is suddenly raised to 760°C. (1,400°F.) It cannot be doubted that the whole column of material would very quickly rise in temperature by the introduction of 4,000 to 5,000 units per ton of iron made. The effect upon the upper portion of the furnace would be to increase the activity of the tendency (designated E) of CO_2 to be reduced to CO, which would neutralise any advantage of the additional heat possessed by the blast. This, indeed, may not be the limit of the evil. CO_2, so decomposed, carries off with it carbon equal in amount to its own; the effect of which is, that a less quantity by so much reaches the hearth to be burnt before the tuyeres.

If the operation in the hearth were one of simple fusion, unaccompanied by any chemical action except that attending the union of the substances which flow off in a melted state, the substitution in the hearth of heat in the blast for one necessarily of a reducing character, viz., that produced by the combustion of carbon, might be permitted; indeed, the temperature of the gases higher up could be kept below that which causes decomposition of the CO_2, by adding more material to be fused at the tuyeres.

SECTION XXXIV.—ON THE PROGRESSIVE CHANGES EXPERIENCED BY THE MINERALS DURING THEIR DESCENT IN THE BLAST FURNACE.

In the preceding pages it has been my object to prove, by actual experiment in the laboratory, as well as by observation at the blast furnace, that as soon as the carbonic oxide generated by the action of the blast on the fuel at the tuyeres has about 30 per cent. of its volume converted into carbonic acid, it ceases to have any action on calcined Cleveland ironstone at the ordinary temperature of the escaping gases of furnaces containing 12,000 to 15,000 cubic feet.

By examining the behaviour of very much larger furnaces than those just named, evidence has been given in favour of the opinion that no addition to a capacity of 15,000 cubic feet is likely to lead to a further reduction of temperature at the top.

The two fundamental laws, viz., temperature, and proportion of CO_2 in the gases, may be considered to constitute a limit of the power of fuel to smelt above a given quantity of iron ore of a specific kind, which, for our present purpose, is assumed to be that afforded by the Cleveland hills.

The practical confirmation of the soundness of this view may be found in experiments 138 and 139, where specimens of this description of ore were exposed, in the gases of a blast furnace, for twenty-four and forty-eight hours respectively, and in neither case was six per cent. of the original oxygen expelled. It is true, a slightly larger proportion of O was removed after an exposure of only two hours in the same gases, but this might easily be accounted for by fluctuations, either in temperature or composition of the contents of the gas-pipe during the period in question; or, what is just as probable, the point of equilibrium was speedily reached, and no further exposure produced any larger amount of reduction.

It by no means, however, follows that a diminution in the quantity of CO_2 contained in the gases as they leave the throat of a particular furnace, nor perhaps, indeed, a diminution in their temperature, would be productive of any economy in the consumption of fuel.

The composition of the gases at the point in question is considered to be determined by a position of equilibrium being established according to the principles laid down in the beginning of Section XV., and in the remainder of that portion of this work experimental proof is instanced of the effect of increased temperature in altering the nature, but not interfering with the existence, of this equilibrium. This naturally leads to a consideration of the changes which the materials experience as they become exposed to greater heat, and to gases richer in carbonic oxide than are to be found nearer the summit; and as this, no less than the final composition of the gases, probably influences the working of the furnace, the progressive nature of these changes invests their study with importance as well as with interest.

If we desire to exhibit, by analysis of specimens of ore, the extent to which reduction of a general character has been effected at any particular depth of the furnace, many difficulties beset the enquiry. There is little doubt channels may and do exist in the materials which will perceptibly modify the nature of the chemical action, when compared with that taking place where the ironstone lies more compactly and, therefore, is much less easily penetrated by the ascending current of deoxidizing gas.

The construction of the furnaces working with closed tops prevents the plans of M. Ebelmen and Professor Tunner being employed for procuring specimens which have been exposed to the action of the gases, even were the objection of retarded access, formerly alluded to, removed. There is, besides this, another inconvenience attending the method practised by these metallurgists which doubtless would interfere with the correctness of the results. It will be remembered that their process consisted in allowing a perforated box containing fragments of ore to descend with the contents of the furnace to any given level, and then by means of a chain and windlass to draw it up through the materials. Looking at the rapidity with which recently reduced iron attracts oxygen, it seems probable that this substance, highly heated as it would become in the lower levels of the furnace, where a moderate quantity of carbonic acid only is present, would incur risk of being re-oxidized to some extent during its passage through the upper zone, where this gas is much more abundant.

A better plan, it appeared to me, consisted in exposing samples of the ore to the action of the reducing gas at various depths of the furnace by means of apertures pierced in its sides. The results of these trials were given in Section X., two hours being the time occupied in each. Even here all source of error was not absent; owing firstly, to the fluctuating and uncertain composition of the gases, and secondly, to the possibility of oxygen being absorbed if the specimens were withdrawn in a heated state, or their composition being altered if cooled in an atmosphere similar to that in which, at a higher temperature, the experiments had been conducted.

In a furnace of 48 feet (Clarence) the following numbers were obtained from calcined Cleveland ironstone:—

Exp.	Depth from top.	Vols. CO_2 per 100 Vols. CO. Average.	Temperature.	Percentage O removed.
160	4 ft. 3 in.	22·75	No signs of redness.	13·70
161	do.	do.	do.	10·04
166	9 „ 9 „	7·25	Cherry red	76·20
171	15 „ 7 „	2·0	Bright red	76·30
172	do.	do.	do.	71·26
177	21 „ 5 „	3·5	Very bright red	68·20
178	do.	do.	do.	81·76
183	27 „ 3 „	5·5	do.	68·10
184	do.	do.	do.	73·83

At a furnace of 80 feet in height (Wear) specimens were similarly exposed, and the loss of oxygen is exhibited in the figures annexed:

Exp.	Depth from top.	Vols. CO_2 per 100 Vols. CO. Average.	Temperature.	Percentage O removed.
188	25ft. 11in.	6·6	Bright red 860°C	84·6
192	52 0	2·33	Very br. red 1,000 to 1,200C	81·0
196	70 4	0·0	White heat	81·8

To the objection, already spoken of, as applicable to the mode of procedure followed in the experiments just enumerated, must be added the circumstance that the conditions of exposure do not exactly resemble those of the furnace itself, where the oxide of iron instead of being isolated, is surrounded on every side by carbon, and by lime, or by this earth, partly or wholly saturated with carbonic acid.

This consideration induced me to suppose that the progressive changes experienced by the minerals during their descent in the blast furnace could be more correctly ascertained by a series of examinations of the gases taken at different levels at different times. In this plan, by comparing the quantity of oxygen they contain with that due to the associated nitrogen, an idea may be had of the extent to which O is contributed by the minerals. This idea is, however, only approximate, because not only have we (*vide* Sec. XXVI.) the quantity of N disturbed by the generation and decomposition of cyanogen, but O is contributed, due neither to atmospheric air nor minerals, but to moisture, or the accidental admission of H_2O. To add to the complexity of the problem, the composition of the gases may be modified by the condition of the materials over which they last passed before being collected for examination. Thus, when the proper state of the ore under treat-

ment comes up for consideration, examples will be given, showing how reduction may be retarded by over-calcination. Suppose a mass of Fe_2O_3 in such a condition as regards roasting to be lodged adjacent to an aperture where the samples of gas for analysis were being collected. It is obvious the latter might be charged with more oxygen than the average of the gases in that zone, owing to the ore generally being in a more advanced state of reduction than the mass, which, to some extent, was affecting the specimens in question.

As has been remarked upon a previous occasion, it is only after many analyses have been made, that irregularities are detected, and then explanation must be sought by appealing to the known properties of the substances under examination.

To assist in the object in view, the following trials were made of the gases from Wear furnace, 80 feet high, and containing 17,500 cubic feet, when the consumption per ton of iron was 12·8 cwts. of limestone, and 23·5 cwts. of coke, containing 10 per cent. of ash, &c.* Furnace making No. 3 iron.

Example No. 1.

A. Exp. 536.—Composition by weight of escaping gases, omitting H.—

CO_2	14·9	= carbon	4·06	+ oxygen	10·84			
CO	28·2	= „	12·08	+ „	16·12			
N	56·9					nitrogen		56·9
	100·		16·14		26·96			56·9

Carbon in gases per ton of iron :—

Coke used	23·5 cwts., less ash, &c.	2·35	= C	21·15
C in	12·8 „ limestone			1·53
				22·68
Less C dissolved in iron				·60
			cwts.	22·08

* For facility in reference, the *Examples* will be numbered consecutively. Occasionally small differences in the calculations which follow may be detected, according to the number of decimal figures employed. These differences, however, do not affect the argument.

Weight of gases per ton of iron, omitting H and H_2O.

		Carbon.	Oxygen.
Nitrogen (16·14 : 56·9 :: 22·08 :)	77·84		
Carbonic acid (56·9 : 14·9 :: 77·84)	20·38	= 5·56	14·82
Carbonic oxide (56·9 : 28·2 :: 77·84)	38·57	= 16·52	22·05
		22·08	36·87

Comparison of O per ton of iron with that due from the various sources:—

Blast brought in with 77·84 nitrogen ...	23·25	
Moisture in blast, say	·66	
Contributed by ironstone	9·00	
Do. limestone	4·09	... 37·00
Difference for experimental error		·13

The oxygen contributed by the ore is considered to be derived as follows:—

Separable at moderate temperature.		
The oxygen combined with 18·6 Fe in the ton of pig ...		7·97
Requiring intense temperature for separation.		
The oxygen combined with ·30 P in P_2O_5 ...	·39	
Do. do. ·02 S in SO_3 ...	·03	
Do. do. ·28 Si in SiO_2 ...	·33	
Do. do. Ca to form Ca S in slag	·28	... *1·03
		9·00

The next trial is of the gas taken from an aperture 16½ feet from the top.

B. Composition of gases by weight.—

			Carbon.		Oxygen.	Nitrogen.
Exp. 537.	CO_2 ...	4·4	= 1·20	+	3·20	
	CO ...	30·8	= 13·20	+	17·60	
	N ...	64·8				64·8
		100·	14·40		20·80	64·8

77·84 being the N per ton of iron, as shown in *A*, we have—

For carbon in gases (64·8 : 14·31 :: 77·84 :) ...	17·29
„ oxygen in do. (64·8 : 20·89 :: 77·84 :) ...	25·09

*By error, the quantity of O was calculated on ·48 cwt. of Si, which includes the "slag" in the pig iron. The actual quantity of Si, as such, is only about ·28. The difference does not affect the calculations based on the statement; the total quantity of oxygen supplied, by the mineral, for reasons given, being partly assumed.—*Vide* Section XXVIII.

C. Composition of gases by weight at 26 feet from top.—

				Carbon.		Oxygen.	Nitrogen.
Exp. 538.	CO_2	... 6·7	=	1·83	+	4·87	
	CO	... 27·8	=	11·91	+	15·89	
	N	... 65·5					65·5
		100·		13·74		20·76	65·5

Carbon per ton of iron in gases (65·5 : 13·74 :: 77·84 :) ... 16·33
Oxygen do. do. (65·5 : 20·76 :: 77·84 :) ... 24·71

D. Composition of gases by weight 39 feet from top.—

				Carbon.		Oxygen.	Nitrogen.
Exp. 539.	CO_2	... 3·5	=	·96	+	2·54	
	CO	... 31·6	=	13·54	+	18·06	
	N	... 64·9					64·9
		100·		14·50		20·60	64·90

Carbon per ton of iron in gases ... (64·9 : 14·50 :: 77·84) ... 17·42
Oxygen do. do. ... (64·9 : 20·60 :: 77·84) ... 24·69

E. Composition of gases by weight 52½ feet from top.—

Exp. 540.	CO_2	... 1·4	=	·38	+	1·02	
	CO	... 34·1	=	14·61	+	19·49	
	N	... 64·5					64·5
		100·		14·99		20·51	64·50

Carbon per ton of iron in gases (64·5 : 14·99 :: 77·84 :) ... 18·09
Oxygen do. do. (64·5 : 20·51 :: 77·84 :) ... 24·72

F. Composition of gases by weight 65 feet from top.—

				Carbon.		Oxygen.	Nitrogen.
Exp. 541.	CO_2	... 0·5	=	·13	+	·37	
	CO	... 34·6	=	14·83	+	19·77	
	N	... 64·9					64·90
		100·		14·96		20·14	64·90

Carbon per ton of iron in gases (64·9 : 14·96 :: 77·84 :) ... 17·98
Oxygen do. do. (64·9 : 20·14 :: 77·84 :) ... 24·14

G. Composition of gases by weight 70½ feet below top.—

				Carbon.		Oxygen	Nitrogen.
Exp. 542.	CO_2 ...	0·0	=	0·0	+	0·0	
	CO ...	34·8	=	14·91	+	19·89	
	N ...	65·2					65·20
		100·		14·91		19·89	65·20

Carbon per ton of iron in gases, (65·2 : 14·91 :: 77·84 :) ... 17·80
Oxygen do. do. (65·2 : 19·89 :: 77·84 :) ... 23·74

H. Composition of gases by weight at tuyeres 76½ feet from top.—

				Carbon.		Oxygen.	Nitrogen.
Exp. 543.	CO_2 ...	2·6	=	·71	+	1·89	
	CO ...	34·7	=	14·87	+	19·83	
	N ...	62·7					62·70
		100·		15·58		21·72	62·70

Carbon per ton of iron in gases ... (62·7 : 15·58 :: 77·84 :) 19·35
Oxygen do. do. (62·7 : 21·72 :: 77·84 :) 26·97

Example No. 2.

After a lapse of two days, when the Wear furnace was working with the same proportions of minerals as upon the previous occasion the gases were again sampled and subjected to examination. Quality of iron, average number, 2·6.

A. Escaping gases assumed to be the same in composition as before. Nitrogen, per ton of iron, therefore, 77·8 cwts.

B. An accident happening to the tube containing the specimen of gas from the aperture, 16½ feet from top, its composition was not ascertained.

C. Composition of gases by weight, 26 feet from top.

				Carbon.		Oxygen.	Nitrogen.	
Exp. 544.	CO_2	5·5	=	1·5	+	4·0		
	CO	32·4	=	13·88	+	18·52		
	N	62·1					62·1	
		100·		15·38		22·52	62·1	

Carbon per ton of iron in gases ...(62·1 : 15·38 :: 77·8 :) 19·28
Oxygen do. do. ...(62·1 : 22·52 :: 77·8 :) 28·21

D. Composition of gases by weight, 39 feet from top :—

				Carbon.		Oxygen.	Nitrogen.
Exp. 545.	CO_2	3·8	=	1·04	+	2·76	
	CO	35·6	=	15·26	+	20·34	
	N	60·6					60·6
		100·		16·30		23·10	60·6
Carbon per ton iron in gases ...(60·6 : 16·30 :: 77·8 :)							20·92
Oxygen do. do. ...(60·6 : 23·10 :: 77·8 :)							29·65

E. Composition of gases by weight, 52½ feet from top :—

				Carbon.		Oxygen.	Nitrogen.
Exp. 546.	CO_2	0·0	=	0·0	+	0·0	
	CO	34·9	=	14·97	+	19·93	
	N	65·1					65·1
		100·		14·97		19·93	65·10
Carbon per ton of iron in gases ...(65·1 : 14·97 :: 77·8 :)							17·88
Oxygen do. do. ...(65·1 : 19·93 :: 77·8 :)							23·81

F. Composition of gases by weight, 65 feet from top :—

				Carbon.		Oxygen.	Nitrogen.
Exp. 547.	CO_2	1·1	=	·3	+	·8	
	CO	33·9	=	14·53	+	19·37	
	N	65·					65·00
		100·		14·83		20·17	65·00
Carbon per ton of iron in gases ...(65·0 : 14·83 :: 77·8)							17·75
Oxygen do. do. ...(65·0 : 20·17 :: 77·8)							24·14

G. Composition of gases by weight, 70½ feet from top.

				Carbon.		Oxygen.	Nitrogen.
Exp. 548.	CO_2	2·3	=	·63	+	1·67	
	CO	36·2	=	15·52	+	20·68	
	N	61·5					61·5
		100·		16·15		22·35	61·5
Carbon per ton of iron in gases ...(61·5 : 16·15 :: 77·8 :)							20·43
Oxygen do. do. ...(61·5 : 22·35 :: 77·8 :)							28·26

H. Composition of gases by weight at tuyeres.—

				Carbon.		Oxygen.	Nitrogen.
Exp. 549.	CO_2 ...	2·8	=	·76	+	2·04	
	CO ...	34·8	=	14·92	+	19·88	
	N ...	62·4					62·4
		100·		15·68		21·92	62·4

Carbon per ton of iron in gases, (62·4 : 15·68 :: 77·8 :) ... 19·55
Oxygen do. do. (62·4 : 21·92 :: 77·8 :) ... 27·33

Example No. 3.

In the following *Example*, taken also from the Wear furnace, the burden of mine being the same as before, the coke is also taken at 23·5 cwt. per ton, but instead of raw limestone being employed as a flux, 10 cwt. of this substance, in a calcined state, was consumed per ton of iron, considered, however, still to contain 1·5 cwt. of CO_2.

The use of calcined limestone, of course, will affect the composition of the gases in the upper portion of the furnace where the CO_2 of the limestone, when employing this material in its raw state, is expelled. I know of no reason, however, why, this region being passed, the gases should be affected by the change.

Analyses were made upon four different occasions, upon as many different days, the particulars of each of which are given, and the calculations are based upon the average.

A. Composition of gases by weight at top :—

	CO_2.	CO.	N.	Quality of Iron.
Exp. 550. ...	7·16 ...	32·82 ...	60·02 ...	No. 4.
„ 551. ...	7·90 ...	33·10 ...	59·00 ...	„
„ 552. ...	8·8 ...	32·5 ...	58·7 ...	„
„ 553. ...	7·8 ...	33·7 ...	58·5 ...	„
Average ...	7·91	33·03 ...	59·06	

			Carbon.		Oxygen.	Nitrogen.
CO_2	7·91	=	2·16	+	5·75	
CO	33·03	=	14·16	+	18·87	
N	59·06					59·06
	100·		16·32		24·62	59·06

Carbon in gases per ton of iron :—

Coke used 23·5 less ash, &c.,	2·35	21·15
Carbon in calcined lime, say		·41
		21·56
Carbon dissolved in iron		·60
	Cwts.	20·96

Weight of gases per ton of iron, omitting H and H_2O :—

		Carbon.	Oxygen.
Nitrogen (16·32 : 59·06 :: 20·96 :)	75·85		
Carb. acid (59·06 : 7·91 :: 75·85 :)	10·16	= 2·78	7·38
Carb. oxide (59·06 : 33·03 :: 75·85 :)	42·42	= 18·18	24·24
	20·96		31·62

Comparison of oxygen per ton of iron with that due from the various sources :—

Blast brought in with 75·85 nitrogen	22·65	
Moisture in blast	·65	
Contributed by ironstone	9·00	
„ limestone	1·09	33·39
Difference for experimental error		1·77

The mode hitherto pursued to obtain an average representation of the composition of the escaping gases consisted in taking samples over a consecutive period of three or four hours, which usually afforded results corresponding pretty closely with the estimated constitution as regards oxygen and carbon. In the present instance, only four specimens of gas were taken on four different days, and the deficiency (1·77) of oxygen leads to the inference that the CO_2 is understated, and that probably the average composition would be :—

		Carbon.	Oxygen.
Nitrogen	75·85		
Carbonic acid	15·00	4·09 +	10·91
Carbonic oxide	39·36	16·87 +	22·49
		20·96	33·40

which will be assumed as the actual composition of the escaping gases.

To avoid a repetition of figures, the quantities of oxygen and carbon associated with the quantity of nitrogen, considered as

equivalent to each ton of iron, will be found in the two subjoined tables, and the analyses made on two different days of the gases from which they were calculated are also given:

			Composition of gases by weight.				Weight per ton of iron.		
				CO_2	CO.	N.	O.	C.	N.
		A At top*					33·40	20·96	75·85
Exp.	554	*B* 16½ from	do.	3·44	33·65	62·91	26·19	18·53	,,
,,	555	*C* 26	,,	1·06	34·97	63·97	24·55	18·15	,,
,,	556	*D* 39	,,	1·72	34·75	63·53	25·21	18·36	,,
,,	557	*E* 52¼	,,	2·36	34·90	62·74	26·24	18·92	,,
,,	558	*F* 65	,,	·79	35·82	63·39	25·13	18·62	,,
,,	559	*G* 70½	,,	0·00	36·63	63·37	25·07	18·79	,,
,,	560	*H* at tuyeres		1·16	37·53	61·31	27·56	20·27	,,

Example No. 4.

The next series of experiments gave the following numbers:

			Composition of gases by weight.				Weight per ton of iron.		
				CO_2.	CO.	N.	O.	C.	N.
		A At top*					33·40	20·96	75·85
Exp.	561	*B* 16½ from top		3·51	32·88	63·61	25·43	17·94	,,
,,	562	*C* 26	,,	1·16	34·69	64·15	24·43	17·96	,,
,,	563	*D* 39	,,	1·55	34·87	63·58	26·01	18·35	,,
,,	564	*E* 52¼	,,	—	Spoilt	—	—	—	
,,	565	*F* 65	,,	·78	35·90	63·32	25·23	18·52	,,
,,	566	*G* 70½	,,	0·00	37·60	62·40	25·70	19·55	,,
,,	567	*H* at tuyeres		1·16	37·70	61·14	27·74	20·43	,,

For facility of comparison, the oxygen of the four sets of analyses just given are placed underneath side by side, and a similar arrangement is adopted with regard to the carbon.

		Oxygen per ton of iron. Limest. Raw. Limest. Calcined.				Carbon per ton of iron. Limest. Raw. Limest. Calcined.			
	Examples	1.	2.	3.	4.	1.	2.	3.	4.
A	At top, cwts.	36·87	36·87	33·40	33·40	22·08	22·08	20·96	20·96
B	16½ from top, ,,	25·09	—	26·19	25·43	17·19	—	18·53	17·94
C	26 ,,	24·71	28·21	24·13	24·48	16·33	19·28	18·15	17·96
D	39 ,,	24·69	29·65	25·21	26·01	17·42	20·92	18·36	18·35
E	52¼ ,,	24·72	23·81	26·24	—	18·09	17·88	18·92	—
F	65 ,,	24·14	24·14	25·13	25·23	17·98	17·75	18·62	18·52
G	72½ ,,	23·74	28·26	25·07	25·70	17·80	20·43	18·79	19·55
H	76½ ,,	26·97	27·33	27·56	27·74	19·35	19·55	20·27	20·43

The phenomenon of a decrease of oxygen as the gases leave the tuyeres when compared with the atmospheric nitrogen, was alluded to in Section XIX., and reference was made to the explanations respecting its cause given by Ebelmen and others. These explanations were, it will be remembered, regarded as unsatisfactory by Dr. Percy, who himself considered the decrease to imply "an abstraction of oxygen from the gaseous current, and its fixation in

* Composition obtained by corrected estimate previously given.

a solid state of combination, or an evolution of nitrogen in sensible quantity from the solid contents of the furnace;" but he adds that he cannot understand how either of these can occur, believing that neither the traces of O nor N which may exist in the fuel can account for the facts observed.

Dr. Percy, in his remarks on the decrease of oxygen in proportion to the atmospheric nitrogen, makes no allusion to the alteration in the quantity of carbon judged by the same standard. Not being acquainted with the composition of the fuel employed in the cases which are quoted by that author, I have not been able with sufficient accuracy to construct tables by which the component parts of the gases are referred to the ton of iron. Nor is this refinement necessary, I have, therefore, simply selected four of his examples where the composition is given of specimens of gas taken near the tuyeres, and at different levels up to the top or thereabouts, and to the volume of nitrogen as given by Dr. Percy, I have added the volume of oxygen and carbon vapour, omitting marsh gas, which is, in all probability, due to volatile matter in the fuel.

Clerval furnace; using charcoal; authority—EBELMEN.

	N.	O.	C. vapour.
At mouth	57·79	24·63	36·39
4½ feet below mouth ...	57·80	25·08	36·30
8¾ „ do. ...	58·15	25·08	36·41
13 „ do. ...	59·14	22·95	37·04
17½ „ do. ...	60·54	19·05	35·87
18½ „ do. ...	63·07	17·50	35·01
22½ = 1½ feet above tuyeres	56·08	21·10	41·90

Clerval furnace; using charcoal; authority—EBELMEN.

	N.	O.	C. vapour.
Below mouth, 3¼ feet ...	57·22	24·33	36·66
do. 9¾ „ ...	60·92	19·92	35·70
do. 19¾ „ ...	63·04	18·01	35·54
do. 28 „ ...	61·22	18·77	37·55
At tymp	58·17	20·86	40·79

Furnace at Eisenerz; fuel, charcoal.—TUNNER AND RICHTER.

		N.	O.	C. vapour.
Below mouth,	11 feet	70·50	22·94	29·50
do.	17 „	71·36	23·24	28·69
do.	23 „	68·81	20·39	31·19
do.	27 „	66·66	18·01	33·34
At tuyeres	34 „	66·34	22·63	33·66

Furnace at Seraing; fuel, coke; authority—EBELMEN.

		N.	O.	C. vapour.
Below mouth,	1 foot	57·06	25·69	40·00
do.	4 „	59·64	23·88	37·91
do.	9 „	62·46	18·48	35·42
do.	10 „	61·67	18·68	36·28
do.	11¾ „	61·34	18·25	36·40
Near tuyeres	45 „	54·63	22·52	45·05

The figures as they stand show incontestably that as a certain volume of gas ascends, it loses oxygen, as has been already pointed out by different writers, but in addition to this, the experiments of these continental chemists confirm what has been advanced in these pages, that there is a simultaneous disappearance of carbon.

To return to the examples afforded by the Wear furnace already referred to, if we compare the quantity of oxygen in the gases at the tuyeres, with that due to so much atmospheric nitrogen, and the carbon with that introduced into the furnace diminished by the reduction of CO_2, as explained in Section XXVIII., we should, in the four analyses of the Wear furnace gases, find both O and C in excess.

For this purpose of comparison, it will be convenient to consider the position of affairs by the time the gases have travelled from the tuyeres to *F*, a distance of 11½ feet higher up the furnace. This point is selected because it will be observed that the oxygen has arrived at its minimum, and the carbon after this also commences to increase slightly, to suffer a still greater diminution as the gases ascend, from a cause quite different, I imagine, from the one we are about to examine.

The loss of oxygen and carbon between *H* and *F* is as follows:—

		Oxygen,	Carbon.
Example	1	2·83 cwts.	1·37 cwts.
„	2	3·19 „	1·80 „
„	3	2·43 „	1·65 „
„	4	2·51 „	1·91 „
Average		2·74 „	1·62 „

The undoubted disappearance of carbon from the gases of the furnace as they leave the hearth, leads us necessarily to enquire whether it may not throw some light upon the simultaneous diminution in the quantity of oxygen.

From what has preceded in previous sections, it might be suggested that this disappearance of C from the gases might be due to its precipitation from the CO. We have only, however, to refer to what has been said on the dissociation of CO to be satisfied that the splitting up of this gas at the temperature which prevails in the lower part of the furnace is impossible, at all events, to any marked extent, (*Vide* Exps. 228, 229, 370, 371, and 372). Moreover such a change could be only of a temporary kind, and would be followed by the carbon re-appearing in its vaporous state; hence the inference that it must have entered into combination with some other element, and in the form of a solid has escaped detection in the ordinary mode pursued in analyzing the gases.

The form of combination into which the missing carbon has entered, I venture to suggest, is chiefly cyanogen, and possibly to some extent carbonic acid, both united with the alkaline metals, which I have shown abound in the lower region of the blast furnace.

I am not acquainted with any previous experiments on the production of the above-mentioned compound of carbon and nitrogen in the blast furnace, which indicate that it ever occurs in any considerable quantity, and Dr. Percy concludes that the idea propounded by Bunsen and Playfair, that it played an important part in the smelting of iron, could not be maintained by reason of the small amount given by these experimenters, viz., 4 grammes per cubic mêtre, or less than 30 kilogrammes per ton of iron.

The question, therefore, which presents itself for consideration is —does there exist any evidence of so large a quantity of cyanogen

being present in the furnace as that represented by the 1·62 cwts. of carbon removed from the gases, which is equal to 3.51 cwt., or 179 kilogrammes of Cy for each ton of iron produced.

In Section XXVI. several trials are described, undertaken with the hope of ascertaining what quantity of Cy was to be found in each cubic mêtre of gas (0°C 760 m. m.) passing up the furnace. Exps. 488 and 493 to 498, give the weight in grammes of Cy per cubic mêtre in the gases, taken at an orifice 8 feet from the tuyeres, and, therefore, about midway in point of cubic content between the tuyeres and the aperture *F*. Among these it will be seen, on reference, that instead of the 4 grammes of MM. Bunsen and Playfair, as much as 49·06, 20·61, 19·00, and 17·32 grammes respectively of Cy were estimated to be present in each *c. m.* and reasons given for considering the actual quantities rather understated than otherwise. Now, if we assume 4,500 cubic mêtres of gas per ton of iron the above named estimated weight of 3·51 cwts. of Cy gives about 40 grammes per cubic mêtre, which is below the quantity ascertained to have been present upon one occasion.

Admitting then the probability that the 1·62 cwts. of carbon has assumed the form of 3·51 cwts. of cyanogen, it remains to consider in what way this action has led to a still more marked change in the quantity of oxygen, viz., 2·74 cwts.

Having regard to the circumstance that the iron is introduced at the top of the blast furnace in the form of an oxide, it is perhaps only reasonable to enquire, before looking for another source of the O which manifests itself at the bottom, whether this latter is not simply a portion of the original oxygen which the conditions of the upper zones of the furnace have been unable to remove.

It must be remembered that the quantity in question, viz., 2·74 cwts., represents above one-third of the oxygen in the $Fe_2 O_3$ required to produce one ton of pig, and we have, therefore, to consider whether it is probable that the iron should retain so large a proportion of its oxygen while passing through the furnace, a proportion fully equal to constitute $Fe_2 O$.

There can be little doubt the *Example No.* 1 in the tables answers this interrogatory in an unmistakeable manner. Through such a furnace as that at Wear, the materials occupy something like 60 hours in their passage, during which they will have been exposed, judging from the analyses, not less than one-third of this

time, or 20 hours to an atmosphere containing on an average about 3 vols. of CO_2 per 100 of CO. Now it is entirely opposed to the observations recorded in these pages on the action of CO, and mixtures of CO and CO_2 on oxide of iron, that this compound should retain so large a proportion of its original O as 33 to 34 per cent. under the conditions to which it is exposed in the blast furnace during so long a period of time. It may also be remarked, looking at the composition of the gases in the series of analyses which constitute the data of *Example* No. 1, that the quantity of oxygen they contain has not increased from the point *C* to that of *G*, being 44½ feet of the height of the furnace, a fact which leads to the conclusion that already at *C*, the ore in this case has been deoxidized as far as CO is capable of performing this operation, which Exp. 370 showed to be within a mere trace of absolute reduction.

To return to the evolution of cyanogen as one of the primary causes of this increase of oxygen at the tuyeres, there is no doubt, I apprehend, that the mere contact, under any circumstances as to temperature, of nitrogen and carbon as they occur in the blast furnace, would fail to produce union between the two, and that for this purpose the presence of potassium or sodium is indispensable. I have, it is true, failed in my experiments to detect the presence of either, but Bunsen and Playfair* speak distinctly to having obtained traces of one of these metals, or its compound with CO. Whether K or Na may not possibly still be found in the blast furnaces of the North of England, or whether the separation of these metals from their oxides is not simultaneous with, and dependent upon the generation of Cy, I am unable to say. This, however, is of little importance for the present enquiry, which is merely dealing with the amount of oxygen, liberated from K_2O or Na_2O at some period or other, necessary for the production of cyanide of potassium or cyanide of sodium. The weight of O set free in this manner will be 2·16 cwts., being the equivalent for 1·62 C converted into Cy.

Beyond the oxygen which is set free from K or Na at the moment when K Cy and Na Cy are produced, there is that to be taken

* Reports, British Association, 1845.

account of, combined with the P, S and Si, which are found in the iron. These three elements exist as P_2O_5, SO_3, and SiO_2, and in all probability will not be separated from their associated oxygen until the hottest region of the furnace is reached, viz., near the tuyeres. Such, at all events, will be true, as regards the SiO_2, and probably the P_2O_5, which furnish the chief part of the oxygen in question.

The quantities of O representing these three substances were taken at ·75 cwts. To this may possibly have to be added a little O, separated from Ca, to form Ca S. The sum of these four made up the 1·03 mentioned at the beginning of this Section.

There is a third probable source of traces of oxygen, viz.:—that combined with iron, independently of those just given, *i.e.*, O would be given off near the tuyeres were none supplied by Ca O K_2O, Na_2O, P_2O_5, SO_3, or SiO_2. In experiments 370, 371, and 372, it was proved when Fe_2O_3, or perfectly reduced spongy iron were exposed to a current of pure CO, there was, if Fe_2O_3 was employed, a trace of O still left unremoved, and, on the other hand, if the pure metal was the subject of experiment, slight oxidation took place. This quantity of O per ton of metal may be taken at ·15 cwts.

The three items just enumerated (2·16—1·03—·15) amount to 3·34 cwts. of oxygen for each ton of iron which, or the greater part of which, must have been set free in the hearth of the furnace, and the average quantity of the four calculations we are dealing with is 2·74 cwts., *i.e.*, this latter weight is present in the gases at the tuyeres, and has disappeared by the time they have travelled through 11½ feet of the height of the furnace.

What has become of this oxygen? is the question I now propose for examination.

It is incredible that any of the earths of the slag can have parted with any of their oxygen higher up, to re-absorb it in a portion of the furnace, where reduction is at its maximum; for, were it so, the excess of vapourized oxygen would be apparent in the gases, which is not the case. It is, in like manner, impossible that the carbon can have taken it, or it would not have disappeared from the gases.

A small quantity will, of course, flow off into the slag, with the minute amount of iron which, even when a furnace is running foundry iron is carried off unreduced with the earthy constituents

of the materials; but this will only account for a mere fraction of the quantity we are considering.*

The slag also frequently contains traces of K_2O and Na_2O, but in such minute quantities that we may fairly assume this mode of exit will not account for more than a trifle of the weight which has actually disappeared between *H* and *G*.

If the assumption be correct that the generation of Cy is dependent on the presence of an alkaline base, there is nothing extravagant in expecting that the extent to which this compound of C and N may be formed will be liable to considerable fluctuation, according as the accumulated quantity of K_2O or Na_2O may be greater or less at one particular time. Neither is it improbable that small alterations in the temperature of the hearth may greatly modify the conditions most favourable for the production of these alkaline cyanides, and, indeed, may transfer the seat of greatest production from one part of the furnace to another. This appears to me one way to account for the marked disappearance of carbon at the tuyeres, which manifested itself in two series of analyses made of the gases in the Wear furnace, to which I would direct attention.

Example No. 5.—

Composition of gases by weight per ton of iron. Furnace using calcined limestone. Burden same nature as that furnishing specimens in *Examples* 3 and 4, previously given: making No. 3 iron.

				per ton iron.				
Exp.			CO_2	CO	N	O	C	N
568	*A*	At top	as before			33·40	20·96	75·85
569	*B*	16½ ft. from do.	1·80	32·60	65·60	23·04	16·71	„
570	*C*	26 „	1·80	35·00	63·20	25·54	18·58	„
571	*D*	39 „	1·20	33·20	65·60	22·92	16.82	„
572	*E*	52¼ „	1·00	35·30	63·70	24·87	18·32	„
573	*F*	65 „	0·00	35·80	64·20	24·14	18·11	„
574	*G*	70 „	0·00	35·70	64·30	24·05	18·03	„
575	*H*	at tuyeres	1·50	31·50	67·00	21·59	15·74	„

* The slag frequently only contains ·5 per cent. of Fe, probably as Fe O.

Example No. 6.—

The second series is as follows: making No. 2 and 3 iron.

Exp.			CO_2	CO	N	O	C	N
576	*A*	At top	as before			33·40	20·96	75·85
577	*B*	16½ ft. from do.	4·00	36·30	59·70	30·02	21·14	„
578	*C*	26 „	3·30	34·90	61·80	27·40	19·45	„
579	*D*	39 „	3·40	31·70	64·90	24·04	16·97	„
580	*E*	52¼ „	·80	37·00	62·20	26·47	19·59	„
581	*F*	65 „	·50	36·30	63·20	25·32	18·82	„
582	*G*	70 „	0·00	34·40	65·60	22·72	17·03	„
583	*H*	76½ tuyeres	1·30	33·20	65·50	23·05	16·87	„

From these last two *examples* it will be seen how difficult it is, in the face of such figures as they contain, to draw up any general theory which will fit every change which makes itself apparent at a blast furnace. These changes are well known to every intelligent manager to be numerous and sudden, and frequently take place without any apparent cause.

After all, as I have already had occasion to remark, in such a complicated series of never-ending changes which are going on in a blast furnace, it is only by dealing with average results that we can hope to render an account of the general nature of the action going on in its interior. The reasons which have been quoted, I trust, will be accepted as justifying the assertion that cyanogen, by being found in sufficient quantity, may account for the disappearance of carbon, and I will now proceed by tabulating all the results of the previous six *examples* to account for the other phenomena in connection with the change in the quantities of oxyen, but previously to doing this, I will add the particulars of four sets of analyses of gases obtained from the upper part of one of the small furnaces at the Clarence Works, 48 feet high, and containing 6,000 cubic feet, so that for convenience of subsequent reference we may have all the figures at one view.

Example No. 7.—

a. Estimate of composition of gases, from Clarence No. 4 furnace, using 29·40 cwt. of coke and 14 cwt. of limestone; making No. 4 iron.

				Carbon.		Oxygen.
Exp. 584	CO_2	10·50	=	2·86	+	7·64
	CO	31·30	=	13·40	+	17·90
	N	58·20	=		+	
		100·		16·26		25·54

Carbon in gases per ton of iron :—

Coke used	29·40 — 2·55 ash, &c. = C		26·85 cwts.
	C in limestone		1·68
			28·53
	Less C in pig		·60
	C in gases		27·93

Weight of gases per ton of iron, omitting H and H_2O :—

		Carbon.	Oxygen.
Nitrogen (16·26 : 58·20 :: 27·93)	99·85		
Carbonic acid	18·08	4·93	13·15
Carbonic oxide	53·66	23·00	30·66
		27·93	43·81 cwts.

Comparison of oxygen per ton of iron :—

Blast, brought on with 99·85 N ...	29·82	
Moisture in blast	·91	
Contributed by ironstone	9·00	
Do. limestone	4·48	44·21
Difference for experimental error		·40

b. Composition of gases, 9¾ feet from top = weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 585	2·14	36·34	61·52			
„ 586	6·30	33·20	60·50			
Average	4·22	34·77	61·01	... 35·00	... 25·34	... 99·85

c. Composition of gases, 15½ feet from top = Weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 587.	5·04	31·36	63·60			
„ 588.	·60	36·60	62·80			
Average	2·82	33·98	63·20	... 33·95	... 24·32	... 99·85

d. Composition of gases, 2½ ft. from top. = Weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 589.	... 0·0	... 33·66	... 66·34			
„ 590.	... 2·8	... 34·30	... 62·90			
Average	... 1·4	... 33·98	... 64·62	... 31·95	... 23·17	... 99·85

e. Composition of gases, 26¾ ft. from top. = Weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 591.	.. 2·46	... 34·80	... 62·74			
„ 592.	.. 3·10	... 34·60	... 62·30			
Average	... 2·78	... 34·70	... 62·52	... 34·97	... 24·89	... 99·85

Example 8.—

The same furnace was using the same quantity of fuel, and 11 cwts. of calcined limestone calculated to contain 2·02 CO_2. Making No. 3 iron.

	CO_2	CO	N			
Exp. 593.	11·18	... 29·10	... 59·72	CO_2 11·34 = C 3·09 + O 8·25		
„ 594.	11·50	... 30·3	... 58·20	CO 29·70 = C 12·73 + O 16·97		
Average	... 11·34	... 29·70	... 58·96	N 58·96		
				100·	15·82	25·22

a. Carbon in gases per ton of iron.—

Coke used ... 29·40—2·59 ash	= C 26·81 cwts.
C in limestone	·55
	27·36
Less C in pig	·60
C in gases	26·76

Weight of gases per ton of iron, omitting H and H_2O.—

		C	O
Nitrogen (15·82 : 58·96 :: 26·76 :) ...	99·51		
Carbonic acid	19·10	... 5·22	... 13·88
Carbonic oxide	50·25	... 21·54	... 28·71
		26·76	42·59

Comparison of oxygen—

Blast with 99·51 N ...	29·78	
Do. moisture ...	·91	
Do. ore	9·00	
Do. limestone ...	1·47	41·16
Difference, experimental error ...		1·43

b. Composition of gases, 9¾ ft. from top.=Weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 595.	... 2·96	... 36·3	... 60·74			
„ 596.	... 3·10	... 36·0	... 60·90			
Average ...	3·03	36·15	60·82	37·46	...26·82	...99·51

c. Composition of gases, 15½ ft. from top.=Weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 597.	... ·60	... 35·5	... 63·9			
„ 598.	... ·30	... 38·3	... 61·4			
Average	... ·45	... 36·9	... 62·65	... 33·96	... 25·40	... 99·51.

d. Composition of gases, 21½ ft. from top.=Weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 599.	... ·30	... 37·	... 62·7			
„ 600.	... 3·70	... 33·3	... 63·			
Average	... 2·00	... 35·15	... 62·85	... 31·84	... 24·71	... 99·51.

e. Composition of gases, 26¾ ft. from top.=Weight per ton of iron.

	CO_2	CO	N	O	C	N
Exp. 601.	... 2·60	... 36·7	... 60·7			
„ 602.	... 4·10	... 34·6	... 61·3			
Average	... 3·35	... 35·65	... 61·0	... 37·50	... 26·58	... 99·51.

To judge of the nature of the action synoptical tables are annexed, in the first of which is figured the weight of oxygen derived from the minerals at each place in the eight *Examples*, which have been cited

in this section. The quantity of O is estimated from the total quantity in the gases, from which is deducted that associated with so much nitrogen and the probable moisture of the blast. The product ought to be that derived from the ironstone and flux.

The second table contains the weight of carbon estimated to be burnt at the tuyeres, which is calculated by taking that contained in the coke, and deducting the CO_2, formed by reduction and carbon deposition, or supplied by the limestone, and which CO_2 has been brought down to CO by carrying off so much C in the upper part of the furnace. The entire weight of C in the CO_2, due to reduction and carbon deposition was given in Sec. XXXI., and elsewhere as 6·58 cwts. per ton of iron, and the difference between this quantity and that actually found as CO_2 in the gases is the amount of C, considered as reduced from CO_2 to CO.

The first step in the calculation is to estimate the O in the blast and the C burnt at the tuyeres, which are as as follows, both reckoned on the ton of iron :—

Numbers showing oxygen in the blast:—

Example	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.
O with N - -	23·25	23·25	22·65	22·65	22·67	22·67	29·82	29·78
O in moisture -	·66	·66	·65	·65	·65	·65	·91	·91
	23·91	23·91	23·30	23·30	23·32	23·32	30·73	30·69

Numbers showing carbon estimated to be burnt at the tuyeres:—

Example		No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
C in coke	cwts.	21·15	21·15	21·15	21·15	21·15	21·15
C in limestone	1·53	1·53	·41	·41	·41	·41	
C in CO_2 reduced to CO	1·02	1·02	2·49	2·49	2·49	2·49	
		2·55	2·55	2·90	2·90	2·90	2·90
C burnt at tuyeres		18·60	18·60	18·25	18·25	18·25	18·25
C actually in gases	do.	19·35	19·55	20·27	20·43	15·74	16·87

Example		No. 8.	No. 9.
C in coke		26·85	26·85
Less C in limest.	1·68	·55	
C in CO_2 reduced to CO	1·65	3·33 1·36	1·91
		23·52	24·94

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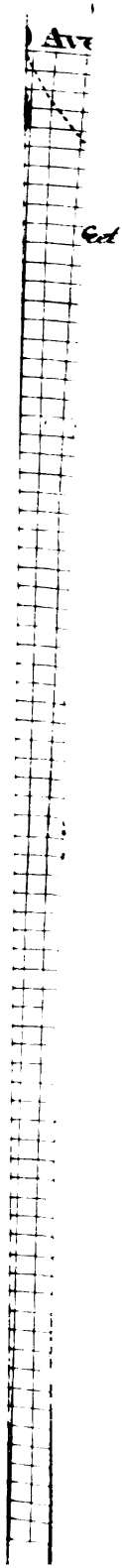


TABLE No. 1, showing cwts. of oxygen per ton of iron contributed by minerals to gases at different depths of the furnace*:—

Example		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
	Furnace Size 17,500 c.ft. Limestone	Wear raw	Wear 17,500 raw	Wear 17,500 calcd.	Wear 17,500 calcd.	Wear 17,500 calcd.	Wear 17,500 calcd.	Clrnce 6,000 raw	Clrnce 6,000 calcd.
A and *a*	Top. Cwts.	12·96	12·96	10·10	10·10	10·08	10·08	13·08	11·90
b	9¾ ft. down	...	...	...	...	...	...	4·27	6·77
c	15½ ...	...	...	...	...	...	...	3·21	3·27
B	16½	1·18	spoilt.	2·89	2·13	−·18	6·70	...	...
d	21½ ...	...	...	...	...	...	...	1·18	1·15
C	26	·80	4·30	1·25	1·13	2·22	4·08	...	...
e	26¾ ...	...	...	...	...	...	...	4·24	6·81
D	39	·78	5·74	1·91	2·71	−1·28	0·72		
E	52½	·81	−·10	2·94	spoilt.	1·55	3·15		
F	65	·23	·23	1·83	1·93	·82	2·00		
G	70½	−·17	4·35	1·77	2·40	·73	−·60		
H	76½	3·06	3·42	4·26	4·44	−1·73	−·27		

TABLE No. 2, showing carbon in excess or deficiency of that burnt at the tuyeres:—

Example		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
	Furnace Limestone	Wear Raw.	Wear Raw.	Wear Calcd.	Wear Calcd.	Wear Calcd.	Wear Calcd.	Clarnc Raw	Clarnc Calcd.
A. and *a.*	Top. Cwts.	3·48	3·48	2·71	2·71	2·71	2·71	4·41	1·82
b.	9¾ ft. down.	...	...	...	...	...	...	1·82	1·88
c.	15½ ,,	...	...	...	...	...	...	·80	0·46
B.	16½ ,,	−1·31	Spoilt	·28	−·31	−1·54	2·89	...	...
d.	21½ ,,	...	...	...	...	...	...	−·35	−·23
C.	26 ,,	−2·27	·68	−·10	−·29	·33	1·20	...	...
e.	26¾ ,,							1·37	1·64
D.	39 ,,	−1·18	2·32	·11	·10	−1·76	−1·28		
E.	52½ ,,	−·51	−·72	·67	Spoilt	·07	1·34		
F.	65 ,,	−·62	−·85	·37	·27	·14	·57		
G.	70½ ,,	−·80	1·83	·54	·30	·22	−1·22		
H.	76½ ,,	·75	·95	2·02	2·18	−2·51	−1·38		

In the hope of rendering the information contained in the preceding figures more intelligible, I have shown them diagrammatically.

The dark perpendicular line in the drawing is the zero point, in respect to excess or deficiency of the quantity of oxygen contributed by the air, including its moisture, and the weight of carbon considered to be burnt before the tuyeres. The faint continuous line shows the carbon, and the dotted one the oxygen. When the

* Where the *minus* sign is prefixed, it signifies that the O present is less than that corresponding to the nitrogen and moisture, and in like manner, in Table 2, the same sign indicates the carbon to be less than that considered as burnt at the tuyeres.

former passes the zero line on the left, and the latter on the right, a *minus* quantity is indicated, *i.e.*, the carbon in the gases is less than that burnt at the tuyeres, and the oxygen is less than that in the blast.

From the two preceding tables an average statement has been prepared, comprising the first four *examples* of Wear. In the first column is set down the quantity of oxygen due from other sources than the blast and its accompanying moisture, and in the second is inserted the carbon in excess or deficiency of the quantity judged to be oxidized at the tuyeres. In addition to this, the changes in the proportions of O and C are laid down in the diagram.

Depth from Top.	Oxygen per ton of Iron.	Carbon per ton of Iron.
A 8 ft. Top ...	Cwts. + 11·53 ...	Cwts. + 3·09
B 16½ „ ...	+ 2·06 ...	— ·45
C 26 „ ...	+ 1·87 ...	— ·49
D 39 „ ..	+ 2·78 ...	+ ·34
E 52¼ „ ...	+ 1·22 ...	— ·19
F 65 „ ...	+ 1·05 ...	— ·20
G 70½ „ ...	+ 2·08 ...	+ ·71
H 76½ Tuyeres ...	+ 3·79 ...	+ 1·47

From the experiments in Section XXVI., we may assume that at or below *F* is the locality where the alkaline cyanides are chiefly generated, and about here also I will consider that the quantity of carbon in the gases instead of being −·20 cwts., is exactly the average of that oxidized at the tuyeres, viz., 18·42 cwts. It will be observed, with this correction, that the carbon increases from *nil* at *E* to 1·47 cwts. at *H*, and the oxygen at the tuyeres is 3·79, but that it never falls in its ascent below 1·05 cwts. in excess of that due to blast.

In this section I have shown that the quantity of cyanogen would account for the largest weight of carbon in excess which appeared at the tuyeres. I will now proceed by endeavouring to explain the probable nature of the changes which give rise to the facts just quoted.

Already at *B*, 16½ ft. from top, at Wear, and at *C*, 15½ ft. from the top, of the small Clarence furnace, we may infer that the ore has parted with all or nearly all the O, which CO can remove, and the limestone with all, or nearly all, its CO_2, for the O in the gases

remains after this pretty stationary in quantity, and the C in the gases is not less when using calcined limestone than when the flux is employed in its raw state.

Granting that the Fe is now all but free from O by the time it arrives at *E*, where it meets with highly heated deposited carbon and nitrogen, together with the K_2O and N_2O, the two alkalies having accumulated by the process described in Section XXVI., the action which results from the concurrence of circumstances, just mentioned, is probably that expressed by the following equation:

$$2\,C + N + K_2\,O^* + Fe_x = C_2\,N\,K_2 + Fe_x\,O$$

in which it will be perceived the Fe is regarded as uniting with the O newly liberated from the alkali. Cyanides no doubt are formed, and their generation cannot fail to be accompanied by oxygen being set free from the alkali, and, from what has preceded, there seems no alternative but to conclude that this oxygen is still in the solid form, and that it is the iron alone which can have absorbed it.

The alkaline cyanide to a small extent is volatilized, for something like 4 grammes of Cy per *c. m.* (18 kilogrammes per ton of iron) is found in the escaping gases, but the chief part being condensed, is carried downwards towards the tuyeres.

We have now the carbon in the form of an alkaline cyanide coming down to the tuyeres, where I conceive it is converted into a carbonate of potash or soda, as the case may be, by the absorption of oxygen. Beyond this oxygen there is that not corresponding with the nitrogen in the hearth at the time, which is also considered to have been fixed by the iron during the generation of the cyanogen and the dissociation of CO, to which must be added that set free from the phosphoric acid, sulphuric acid, silica, and lime, as already mentioned in the present section.

It cannot be expected, under the circumstances of the case, that the figures obtained from the various analyses should correspond very closely with any formula. I shall, therefore, not attempt to do more than merely state that the presence of so large a quantity of cyanogen and alkaline bases appears to me to justify the conclusion that it is to these substances that the apparent excess of carbon and oxygen in the lower region of the furnace has to be attributed.

I may add that I was fully aware that potassium and sodium as

* Or $Na_2\,O$.

carbonates had been found at the tuyeres free from any admixture of cyanides, having myself collected considerable quantities of these compounds which had escaped in a state of fusion. Inasmuch, however, as the actual quantity of carbonic acid was not directly estimated in the experiments on the alkaline cyanides detailed in Section XXVI., the amount of this substance can only be inferred by calculating the weight of alkali which would represent the Cy actually present, and regard the remainder as carbonate. In some instances, there can have been a mere trace of CO_2, as in Exps. 497 and 498, in the former of which about 93 per cent. of the K and Na must have been in the form of cyanides. At the aperture, 8 feet above the tuyeres, six different experiments gave an average of about 80 per cent. of the alkali existing as cyanides, and 20 as carbonate.

Exp. 603. Being desirous of ascertaining by direct experiment the actual quantity of CO_2 present as alkaline carbonate per *c.m.* of furnace gas, I had a hole drilled about 12 inches above one of the tuyeres of the Wear furnace, and from it I obtained 15·22 grammes of carbonic acid per *c.m.* of gas in the form of carbonate of potash and soda.

Many other modes of reaction besides the direct union of C and N in the presence of K or N might be suggested as accounting for the disappearance of C and O from the gases. Thus CO might be split up in the following manner:—

$$2\,CO + N + K_2O + Fe_x = C_2NK_2 + Fe_x\,O_3,$$

and the resulting alkaline cyanide and oxidised iron might then be resolved into the condition of the elements given in the first member of the equation, to be again converted into C_2NK_2 and Fe_x. This reciprocating action might thus go on *ad infinitum*.

Of course, from this round of decomposition and reunion the oxygen evolved from the phosphoric acid, sulphuric acid, silica, and lime would be free, because it being a fresh quantity brought in by every ton of iron produced must, and I have shown does, make its appearance in a constant ratio among the gases.

The formula given above accounts for the fixation of C and O equivalent for equivalent, which is not by any means the uniform proportion observed. The following equation would give one

equivalent of C to two of O, as having passed from the gaseous to the solid form:—

$$2\,CO_2 + N + K_2O + Fe_x = C_2NK_2 + Fe_xO_5,$$

and then

$$C_2NK_2 + Fe_x\,O_5 = \text{at tuyeres } K_2CO_3 + N + CO_2 + Fe_x$$

In all probability it is, however, by no one mode of interchange that decomposition and re-combination are effected, but by several, in which also the cyanogen may possibly assume the form of cyanic acid.

Whether the alkalies exist as carbonates, or in the caustic state at the tuyeres, I am not very certain. The gases in that region always contain some CO_2. At the period when (Exp. 303.) 15·22 grammes per *c.m.* of this acid was in the form of alkaline carbonate, the following was their constitution by weight:—

Exp. 604.	CO_2	...	3·26
	CO	...	35·37
	N	...	61·37

There was also present a large quantity of cyanogen, viz.: 111 grammes per *c.m.*

If the alkalies were caustic in the furnace itself, they would of course absorb CO_2 during the process of absorption by the water used in the experiments for determining the quantity of cyanides.

It ought to be remarked that the conversion of K_2 Cy or Na_2 Cy into K_2CO_3 and Na_2CO_3 need not necessarily be exclusively confined to the neighbourhood of the tuyeres, for it would appear as we ascend in the furnace the proportions of cyanides and carbonates alter, the former decreasing relatively, and the latter increasing. Thus in the experiment for ascertaining the quantity of saline compounds we had the alkaline bases in—

Exp.		As Cyanides.	As Carbonates.
489 *E*, 24 ft. above tuyere		19·75 grms. per *c.m.*	12·24 grms. per *c.m.*
490 *C*, 50½*	„	10·68	15·19
491 *B*, 60*	„	9·14	14·90

Exp. 488 shews that 112·7 grammes of K and Na are present per *c.m.*, which is equal to about 500 kilogrammes, or 10 cwts. per

* In Section XXVI., C and B are erroneously given as 60 and 76 feet from tuyeres instead of 50½ and 60 feet respectively.

ton of iron. It must, however, not be forgotten that this large quantity represents a vast accumulation of these alkaline metals, and that it is the same quantity of these substances which appears over and over again in the lower parts of the furnace. Such also must be the conduct of the apparent excess of carbon and oxygen at the tuyeres, alternately fixed by the potash and soda, and gasified at the tuyeres. With regard to the oxygen, however, it must be remembered that a portion of it is a quantity contributed, not by this reciprocating action, but by a continued supply from the P_2O_5, SO_3, SiO_2, and CaO, estimated at 1·03 cwts. for every ton of iron produced. Confirmatory of this, it will be seen that there is in the gases a weight of oxygen beyond that due the blast, which never, in the average of the four *examples*, falls below 1·05 cwts.

Where the quantity of potassium or sodium is known to exist as mere traces in the raw materials used in the manufacture of iron there is but one way of accounting for the large quantity of these metals present in a furnace which has been in blast for some time, viz., by the process of accumulation formerly alluded to. It follows, therefore, as a matter of course, that in a furnace recently set to work, there having been no time for the operation of this cumulative action, the quantity of K and Na and consequently of the Cy must be small.

The following experiments were made at one of the Clarence furnaces, containing 25,500 cubic feet, which had been blown in a few weeks before the date of the trials.

Per *C mètre* in grammes.	8 feet above tuyeres.		Escaping Gases.	
	Exp. 605.	Exp. 606.	Exp. 607.	Exp. 608.
K ...	... 6·04	... ...	·99	...
Na ...	... 0·32	... ...	·06	...
Cy ...	... 4·25	... 4·34 ...	nil	... nil.
Other substances	6·99		1·74	
Total sol. in H_2O	17·60		2·79	

If the somewhat irregular results exhibited in *Examples* 5 and 6 are to be relied on, it would be erroneous to suppose that this fixation of C and O at a little distance above the tuyeres, and their re-appearing among the gases at the tuyeres is a rule without

any exception. Looking at the diminution merely of the carbon, amounting to 2·51 cwts. per ton of iron in *Example* 5, and 1·38 cwts. in No. 6, one might feel inclined to ascribe the deficiency to the seat of generation of cyanides having been changed, from some local disturbance, at the moment when these two samples were taken, and instead of K Cy and Na Cy being transformed into carbonates, they were in process of being formed. It is to be remarked, however, that instead of there remaining an excess of O as happened in the four previous *examples*, when the C was at its minimum, in *Example* 5 there is also an absorption of 1·73 cwt. of O at the one, and ·27 at the other.

It not unfrequently happens that a furnace suddenly commences to run a black slag, often ascribed, for want of a better reason, to a lump of unfused mass, getting detached from the sides, coming down and imposing on the coke an amount of work beyond its powers. This blackness is generally due to oxide of iron. May it not be that the five tendencies mentioned in Section XV. being disturbed from some slight cause, oxygen other than that liberated from the sources already mentioned is actually absorbed by the iron coming down into the hearth, and that then by a second change in the state of equilibrium, the oxygen thus fixed is rapidly vapourized, possibly by the accumulation of Cy?

In support of this hypothesis, I would direct attention to the occasional abnormal quantities of oxygen which often make their appearance in higher regions of the furnace, as, for example, at *E* and *C* in the two *examples* under examination (Nos. 5 and 6), as well as at *E* in *Example* 3, and *C* and *D* in *Example* 2. Looking at the numbers both above and below these, and at the distance, generally speaking, from the top, where both ore and limestone must have parted with their volatile constituents, the only way to account for the disturbance is by some sudden extrication of O lower down, which O must in the first place, I am supposing, have become fixed by the iron.

Leaving now what may be considered an abnormal state of a furnace working, I propose returning to the four *examples* which formerly engaged attention.

Eventually, the potassium and sodium, in one or other of their forms of combination, escape along with their associated carbon and oxygen at the throat of the furnace, or in the slag, the sum of the

metals being of course exactly that brought in by the materials in which they are only to be found in infinitesimally small proportions.

Following the gases up the furnace, we pass the point *C*, and arrive in a region between it and *B*, where both oxygen and carbon ought to be increasing, because we are in that zone where the last portion of reduction of the Fe_2O_3 is being accomplished, and where CO_2 must be in process of being given off by the limestone. Accordingly we find that the oxygen is really increasing in quantity; but not only has the previous excess of ·34 cwts. of carbon at *D* disappeared, but there is ·49 cwt. of deficiency, so that between *D* and *C* ·83 cwts. of carbon per ton of iron have vanished from the gases.

The only solution to this phenomena, I apprehend, is that afforded by the dissociation of carbonic oxide, by which, saving the minute quantity of O absorbed by the iron in this action, we have two equivalents of CO becoming one of C and one of CO_2, which accounts for carbon disappearing from the gases, and the oxygen, so far as this change itself is concerned, remaining almost the same in quantity.

It must not, however, be supposed that, in the four *examples* just quoted, carbon deposition has ceased because the C now exhibits an increase in the gases. On the contrary, looking at the fact that at all the positions of the furnace which have furnished the data upon which the preceding calculations have been based, the temperature varies from full red to bright red, and this condition of temperature being the least favourable for carbon deposition, this process will continue in very active operation higher up the furnace, where the heat is less intense.

Unquestionably the increasing CO_2 as we ascend offers a certain amount of opposition to the dissociation of CO for reasons already explained, but even at *B*, 9½ feet above *C*, the CO_2 per 100 of the gases was only in the case of

Examples	1	2	3	4
CO_2 ...	4·4 ...	not given. ...	3·44 ...	3·51
to CO ...	30·8 ...	„ ...	33·65 ...	32·88

which is about 12 vols. CO_2 per 100 CO. This is a mixture still very powerful in producing the action under consideration, for in Exp. 307, when calcined Cleveland stone was exposed to furnace

gases containing 19 of CO_2 per 100 of CO, 2·40 per cent. of C, reckoned on the Fe, was deposited.

The opposition caused by the presence of CO_2 to carbon deposition doubtless goes on increasing as the gases ascend, but, on the other hand, the temperature falling rapidly as the throat of the furnace is approached, the conditions for the dissociation of CO will, in all probability, become more favourable. This was clearly proved in the following experiments, given in Section XIII., in which calcined Cleveland stone was exposed for two hours only to the gases in apertures of one of the Clarence furnaces of 6,000 cubic feet.

Exp.	Feet from top.		Temperature.	Vols. CO_2 per 100 CO.	C deposited per 100 Fe.
318.	4	3	No signs of redness ...	21	3·07
319.	9	9	Cherry red ...	5	·56
320.	15	9	Bright red ...	0	·32
321.	21	5	Very bright red	6	·55
322.	27	3	do. ...	9	·32

The composition of the gases being taken at other times may not, and probably does not, agree exactly with that at the period of the experiments.

To what extent carbon deposition proceeds in the furnace after the gases become mixed with CO_2 proceeding from the reduction of the $Fe_2 O_3$, it will be difficult to determine.

It appears pretty clear, however, that dissociation of CO may be going on, between the point *C*, 26 feet below the top, and their escape at the throat, although the gases are passing through carbon sufficiently heated to cause CO_2 to be resolved into CO by C.

I would explain this apparent paradox by the circumstance that after the ironstone enters the blast furnace, being for the most part in large pieces, it is very unequally heated. Thus the centre of a block may be at a low red heat, and yet the exterior be surrounded by carbon at a bright red. In such cases the CO, penetrating as it does the interior of the masses of ore, acts upon the $Fe_2 O_3$ under circumstances, as regards temperature, highly favourable for carbon impregnation, but as soon as the CO_2 generated by the dissociation of CO, which gave rise to the deposition of C, reaches the highly heated coke outside the mass it is resolved into CO.

It may fairly be suggested that the evolved CO_2 in all probability will attack by preference the finely deposited carbon rather than

the solid fuel, both being extremely and equally hot, and in this way the former would not be increased in quantity, inasmuch for a molecule of C deposited in the interior of a block of ironstone, one would be gasified by CO_2 on its exterior. This, however, is scarcely consistent with the known nature of the action; the carbon is chiefly, indeed, it may be said, entirely, deposited in the interior of the lumps of ore, hence the CO_2 is passing through C, the result of dissociation of CO, at a temperature insufficient for the action $CO_2 + C = 2\ CO$ to take place, and in this way those large quantities of deposited carbon, described in Section XI., are produced. Exp. 211, in 4½ hours showed calcined Cleveland stone capable of taking 64 of C per 100 of Fe, which is equal to more than 12 cwt. per ton of pig iron.

I do not pretend to say to what extent, in the blast furnace, the deposition of carbon in the ironstone itself and the consequent gasification of the fuel go on, but I do maintain that the quantity greatly exceeds that indicated at any one part of the furnace by the abstraction of the carbon from the gases. I have been led to adopt this opinion because, after the weight of C disappears from the gases, never much exceeding 2 cwts. per ton of metal, we are only entering the zone where the dissociation of CO is known to be the most active; besides this, we have the whole of the ironstone broken down into a coarse powder by the copious interposition of carbon in its pores, so visible upon occasions when access is had to the interior of the furnace lower down as already described. Indeed so plentiful is this fine carbon that when the walls are pierced, and the gases escape without inflaming, it is expelled from the orifice in a form resembling black smoke.

I would now briefly summarize what I conceive to be the action proper of the blast furnace, *i.e.*, supposing no alkaline substances to be present. This, no doubt, is a condition of things not to be found in practice, but experiment would indicate (*vide* Section XXVI.) that the alkalies, along with their associated cyanogen are not indispensable for the reduction and carburization of iron. This imaginary process would consist in the volatile constituents of the roasted ore, viz., its oxygen, being expelled probably before it has passed the first 10 or 12 feet of the furnace. This is inferred because already at a depth of 16½ feet there is only 2·06 cwts. of oxygen due to the minerals present in the gases, and of this 1·03, or something like it, has been contributed,

not by Fe_2O_3, but by P_2O_5, SO_3, SiO_2, and CaO. The remainder, 1·03 cwts., along with a certain quantity of carbon, ·34 cwts. is probably due to the carbonic acid of the flux, seeing that it requires a higher temperature to split up $CaCO_3$ than to reduce an oxide of iron. From the point *B* in the furnace (*vide* diagram *Example* 1) the oxygen in the gases remains almost stationary until we approach the tuyeres, where the small quantity of O absorbed by the iron in the dissociation of CO, and that combined with the P, S, Si, and Ca, found in the iron and slag alone ought to appear. Here also the quantity of carbon in the gases ought to be that furnished by the coke, less the portion which may have been carried off by the reduction of CO_2 to CO in the manner already described.

Simultaneously with the process of reduction is the deposition of carbon by the splitting up of CO into C and CO_2, and that this takes place very soon after the immersion of the ironstone among the gases, seems to admit of no doubt. This operation of carbon impregnation will continue until the iron or its lower oxide is sufficiently heated to suspend further action, in the manner already fully explained in the sections upon the dissociation of CO.

No doubt, even in this suppositious case of the absence of the alkalies K_2O and Na_2O, there would ensue irregularities in the composition of the gases at the same position in the furnace, which might result from a retarded or accelerated rate of reduction, from the nature of the ore itself, or from some of those mechanical causes which have been spoken of. Substantially, however, I apprehend there would not be found any of those discrepancies, to explain which I have bestowed some pains in this section, and which, in my judgment, are to be entirely attributed to the presence of the alkalies, potash and soda, and the consequent generation of cyanogen.

If I am correct in this supposition, and if the experimental proof of the great fluctuations in the quantities of these substances is to be relied upon, it is not difficult to comprehend that there must necessarily be corresponding irregularities in the character of the products in different parts of the furnace.

I would have willingly directed my attention to further experiment, with the view of confirming, by additional study of the nature of those re-actions which take place in the furnace itself, the opinions which have been advanced in this section, but, I trust

enough has been said to show how difficult this task would be, looking at the next to impossibility of accurately reproducing in the laboratory those conditions, the effects of which it has been my object to describe.

SECTION XXXV. — ON THE BEHAVIOUR OF PHOSPHORUS AND SULPHUR IN THE BLAST FURNACE.

The undoubted evil produced by the presence of phosphorus or sulphur in iron confers an interest upon any fact connected with their action in the blast furnace. It was this consideration which induced me to take, during some days, specimens of all the raw materials being charged into the Wear furnace, and to sample the iron and slag which were obtained when the minerals in question reached the hearth, so as to ascertain, if possible, by careful analysis, the extent to which each found its way into the iron.

It is, perhaps, not very material for the purposes of this enquiry to determine the exact condition in which these two hurtful ingredients exist in the substances under treatment, nevertheless a few words on this subject may be interesting, if not useful.

According to an analysis made by Mr. Dick at the School of Mines,* a specimen of Cleveland ore, dried at 100°C., contained :—

Fe O	39·92
$Fe_2 O_3$	3·60
Mn O...	·95
$Al_2 O_3$	7·86
Ca O	7·44
Mg O	3·82
$K_2 O$	·27
CO_2	22·85
$P_2 O_5$...	1·86
$Si O_2$ soluble in H Cl	7·12
$Fe S_2$	·11
So_3	trace
$H_2 O$ in combination...	2·97
Organic matter	trace
Insoluble residue ($Si O_2$ 1·5, $Al_2 O_3$ ·10, and $Ti O_2$ ·03; Ca O and $Fe_2 O_3$ trace.)	1·64
	100·41

* Geological Survey Great Britain.

The sulphur, with the exception of the trace existing as SO_3, is in such a form, Fe S_2, as will permit its expulsion from its combination by calcination, the products being $Fe_2 O_3$ and SO_2. It is, however, very questionable whether the greater portion of the SO_2 thus generated may not be taken up by the Ca O or Mg O of the ironstone, these earths absorbing sulphurous acid with great rapidity at a red heat.

In respect to the phosphorus, Mr. John Pattinson, of Newcastle, informs me that he considers that this substance does not exist in combination with the iron in the Cleveland ore. This chemist rests his opinion upon the fact that no action was produced upon a specimen of this mineral, containing 2·25 per cent. of phosphoric acid, by sulphide of ammonium, he having previously ascertained that phosphate of iron (vivianite) is decomposed, with formation of phosphate of ammonia and sulphide of iron, on being digested in a solution of this salt. One hundred parts of the ironstone was mixed with as much vivianite as would give one of $P_2 O_5$; the mixture was then treated with sulphide of ammonium, and on the solution being tested, nearly the full quantity of phosphoric acid was obtained.

Either, then, the $P_2 O_5$, if combined with iron, is in such a form as to resist the action of the salt of ammonium; or, what is more probable, this acid is in combination with some other base, and this base, looking at the quantity of organic remains found in this description of ironstone, is probably lime.

In whatever form, however, the phosphoric acid may occur in the mineral, it is certain the act of calcination will not affect its quantity, and it may, therefore, with certainty be inferred that all the phosphorus existing in the bed of ironstone finds its way into the blast furnace.

The specimens of materials collected in the manner already mentioned, were submitted to examination in the following way:—

Exp. 609. *Pig Iron.*—(A)—The method employed to estimate *phosphorus* in pig iron was the following:—A known weight, usually 5 grammes, of clean borings was digested with aqua regia until dissolved, evaporated to dryness on the waterbath, and the residue dissolved in water and filtered from carbon, silica, &c.. The aqueous solution was then heated to boiling, and sodium sulphite cautiously added, until all the iron was reduced to the ferrous condition. A few drops of ferric chloride were then added, and

ammonia dropped in until a precipitate just began to appear. Finally, an acid solution of ammonium acetate was added, and the whole boiled and filtered while hot. The precipitate thus obtained consists of ferric phosphate mixed with more or less of a basic ferric acetate, and contains the whole of the phosphoric acid formed by the oxidation of the phosphorus in the pig iron, provided that sufficient ferric chloride has been added. If too much ferric salt be employed, a voluminous precipitate, difficult to wash, is obtained; but, by very little practice, it is easy to get just such a quantity of precipitate as will contain all the phosphoric acid, without being too bulky to filter and wash well.

This precipitate is dissolved in hydrochloric acid, tartaric or citric acid added, and finally, the whole supersaturated with ammonia. The organic ammonium salt, if present in sufficient quantity, keeps the whole of the iron in solution, even though strongly alkaline. To the cooled liquid, solution of magnesia (magnesium sulphate, or chloride, mixed with ammonium chloride and supersaturated with ammonia) is added. The bulk of the whole should not exceed 100 or 120 ccs. After 24 hours' standing, a more or less coloured magnesium ammonium phosphate has precipitated partly on the sides of the vessel. This precipitate is apt to contain organic matter, iron compounds, and excess of magnesia; but on dissolving it in weak hydrochloric acid (after filtration from the ammoniacal supernatant liquor), and re-precipitation by ammonia in presence of a little tartaric or citric acid, usually there is obtained, on standing for a few hours, a snow-white precipitate of magnesium ammonium phosphate. Should the precipitate not be perfectly colourless, the precipitation may be repeated. Finally, the precipitate is well washed with ammoniacal water, incinerated and weighed as magnesium pyrophosphate.

The original magnesium ammonium phosphate, not being absolutely insoluble in ammoniacal solutions, a certain diminution in the percentage of phosphorus thus found is apt to ensue; but, on the other hand, a slight increase in weight of the precipitate from the precipitation of a little excess of magnesia along with the double phosphate, is apt to occur, the more so the larger the excess of magnesia liquor added in the first instance.

This method of phosphorus estimation, viz., conversion into ferric phosphate, precipitation by acetate, and conversion into magnesium pyrophosphate, is referred to whenever the term "acetate process" is employed.

(B.) In order to estimate the *total carbon* contained, a known weight of borings was digested for 24—48 hours with neutral copper sulphate solution in excess; usually at the end of this time all action had ceased, this point being ascertained by feeling with a glass rod if any hard lumps of metallic iron were still undissolved. The spongy copper, thus precipitated along with the undissolved carbon, was thus collected on a filter of asbestos, well washed, dried, and finally burnt in a stream of oxygen, a red-hot tube containing copper oxide being placed in front of the combustion tube, to ensure the conversion of any CO that might be formed into CO_2; from the weight of CO_2 thus produced the carbon was calculated.

(C.) The *carbon, in a so-called uncombined state*, was estimated by dissolving a known weight of borings in hydrochloric acid, collecting the insoluble portion on an asbestos filter, and burning in a stream of oxygen, as in (B).

By deducting the weight of (C) from that of (B), the quantity of carbon in its so-called combined form is obtained.

(D.) The *sulphur* was estimated by treating a known weight of borings with hydrochloric acid in a flask, furnished with a cork and delivery tube, and passing the evolved gases through a clear solution of potassium plumbate (lead nitrate, super-saturated with caustic potash, and decanted after settling). Towards the end of the operation, the flask was heated to boiling, and kept in gentle ebullition for about half-an-hour. The lead sulphide thus precipitated was rapidly washed, oxidised by a little nitric acid, or by hydrochloric acid and potassium chlorate, diluted and precipitated by barium nitrate or chloride, and finally the barium sulphate produced, after 24 hours' standing, collected and weighed. Owing to the solubility of barium sulphate in acids, a slight loss of sulphur by this process is inevitable, but probably the quantity thus lost is only a small percentage of the amount weighed, and as this does not usually represent nearly so much as 0·5 per cent. of the pig iron, the loss of sulphur is barely appreciable.

In pig irons, containing only traces of sulphur, fairly approximate estimations may be made, by comparing, by the eye alone, the relative black turbidities produced by different samples when all the conditions of the experiment are the same, a small quantity of iron containing a known small percentage of sulphur being taken as a standard of comparison.

(E.) *Silicon and slag insoluble in acids* were estimated by dissolving a known weight of borings in hydrochloric acid, evaporation to dryness at 120° C., re-dissolving in dilute hydrochloric acid, and weighing the substance left, after burning off all the graphitoidal carbon. This weighed substance was then boiled with di-sodium carbonate solution, and the portion insoluble in this menstruum weighed as "*slag*," the difference between this weight and the former one represents Si O_2 dissolved by the carbonate solution; this difference was thus calculated as *silicon*.

This method was adopted as the best at command. It is manifestly open to many objections, *e.g.*; a portion of silicon is stated to exist in some irons in a state where acids do not act on it; hence this silicon would be weighed as slag, sodium carbonate not being capable of dissolving the unoxidized metalloid. On the other hand, a portion of the slag is sure to be attacked by the acid, and consequently an additional quantity of silicon is represented as being present in the metalloidal form, the Si O_2 obtained being increased by this action of the acid; alumina, lime, &c., of this attacked slag being thus left out of consideration altogether.

Possibly, too, siliciuretted hydrogen may be evolved by the action of hydrochloric acid.

(F.) *Metallic iron.*—This was usually obtained by difference; after subtracting from 100 the sum of the percentage of total carbon, phosphorus, sulphur, silicon, and slag the residue was considered to be iron. Evidently, this is only an approximation. Whatever errors are involved in the direct estimations of the other constituents are accumulated in this differential estimate of iron; moreover, other bodies are usually present to a greater or less extent, as manganese,* copper, titanium, &c., &c., and possibly a certain amount of

* Upon a former occasion, I had a series of very elaborate analyses performed in the Clarence laboratory, on Cleveland iron, by Mr. John Pattinson, of which a few are subjoined to show the manganese and other substances present:—

	No. 1.	No. 1.	No. 1.	No. 3.	No. 4.	Mottled.
Fe	93·030	92·68	92·43	93·66	94·64	93·59
C combined	·480	·78	·32	·28	·26	·85
C uncombined	2·830	2·43	3·43	3·13	2·45	2·70
Si	2·310	2·72	1·70	·88	1·87	·66
Mn	0·576	trace	·30	·37	·93	·79
Al	trace	—	—	—	—	—
Ca	—	—	·05	·30	—	·26
Mg	—	—	·01	·02	—	·07
Ti	—	—	·56	·14	—	—
S	·040	·25	·13	·17	trace	·35
P	·300	·30	1·24	1·23	1·00	1·05
	99·566	99·16	100·17	100·18	101·15	100·32

oxygen. Nevertheless, in several instances, direct estimations of the iron by the permanganate method, executed with great care, gave percentages of iron only a few tenths in excess or deficiency of that obtained by the differential method.

Several other methods of estimation were employed for different constituents, but were finally abandoned in favour of those above described. Thus, for total carbon, fine borings were heated in a combustion tube, with a mixture of lead chromate and potassium chlorate, and the CO_2 produced weighed. Sometimes a higher percentage was thus got than by the copper sulphate method, (B). This might be attributed to particles of dust in the chromate, or evolution of chlorine from the chlorate. Usually, however, the numbers thus got were less than those by method (B), owing to the incomplete oxidation of iron otherwise than in very fine powder.

Similarly, sulphur was occasionally estimated by solution of the borings in aqua regia, or in hydrochloric acid, along with potassium chlorate; the acid liquid being nearly neutralized by ammonia, and then precipitated by barium sulphate: the percentage of sulphur thus found, however, was always much less than that got by the hydric-sulphide process (D); and in many cases, when (D) indicated appreciable quantities of sulphur, none whatever was found by the aqua regia or hydrochloric acid and chlorate process.

A few experiments were made on the estimation of phosphorus by molybdic acid; but, either from impurity in the molybdic acid, or other causes, in some instances, scarcely any phosphorus could be found by this method in samples containing 1·5 per cent., although the quantity of molybdic acid added was upwards of 1,000 times the weight of phosphorus present.

In the estimation of silicon and slag, no great difference in the result appeared to ensue, whether hydrochloric acid, aqua regia, or nitric acid were employed as solvents in the first instance.

In estimating the amounts of phosphorus and sulphur received from the furnace, average samples in the pig iron were estimated by methods (A) and (D) above described.

Exp. 610. *Ironstone.*—A known weight was boiled with hydrochloric acid, and the filtered solution treated exactly as the ferric solution obtained from pig iron in method (A).

Exp. 611. *Slag.*—A known weight was fused with a mixture of potassium nitrate and di-sodium carbonate, and the product dissolved in hydrochloric acid, and filtered from silica. From part of this solution the sulphur was precipitated as sulphate by barium nitrate. Another portion was examined for phosphorus by the "acetate process" (A). In this case, a correction was made on the weight of barium sulphate obtained, on account of the presence of a small quantity of sulphate in the weighed quantity of alkaline salts employed for the fusion.

Exp. 612. *Limestone.*—Dissolved in nitric acid and evaporated to dryness: residue taken up by hydrochloric acid, and the solution thus got, treated as the similar solution got with the slag.

Exp. 613. *Coke.*—Fused with a known weight of nitrate and carbonate mixture, and the sulphur precipitated by barium, as with the slag; corrections being made for the sulphate in the alkaline salts used.

The results of the determinations conducted in the manner described were as follows:—

	Phosphorus.	Sulphur.
Calcined ironstone contained per cent. ...	·522 ...	1·052
Limestone ... „ „ ...	·011 ...	·059
Coke ... ... „ „ ...	·265 ...	1·580
Pig iron ... „ „ ...	1·441 ...	·093
Slag ... ... „ „ ...	·098 ...	2·633

The consumption per 100 of iron was as follows:—

Calcined ironstone, 240 ... Limestone, 60 ... and Coke, 120

And taking the slag at 150 per 100 of pig iron we have:—

Phosphorus in 240 of calcined ironstone at	·522	= 1·253 pr 100 of iron.	
„ „ 60 „ limestone	„ ·011	= ·007	„
„ „ 120 „ coke	„ ·265	= ·318	„
Total phosphorus entering furnace per 100 of iron		1·578	

Phosphorus leaving furnace in				
100 of pig iron at 1·441%		1·441		
„ „ 150 „ slag	„ ·098	·147	1·588	„
Apparent excess leaving the furnace ...			·010	„

Sulphur	in	240 of calcined ironstone	at 1·052 = 2·525	pr 100 of iron	
„	„	60 „ limestone	„ ·059 = ·035	„	
„	„	120 „ coke	„ 1·580 = 1·896	„	
Total sulphur entering furnace per 100 of iron				4·456	
Sulphur leaving furnace in					
		100 of pig iron at ·093% = ·093			
„	„	150 „ slag	„ 2·633 = 3·950	4·043	„
Apparent excess entering the furnace ...				·413	„

If the figures in the preceding statement are correct, it would appear the whole of the phosphorus entering the furnace is accounted for, and that almost exactly one-tenth of this substance finds its way into the slag, and the remainder into the iron.

As regards the sulphur, it would seem that the act of calcination has not only not freed the ironstone of any of this ingredient, but comparing the quantity in the roasted ore with that in any analyses of the raw stone, there is a positive increase. This would rather favour the belief that the lime or the magnesia has absorbed the sulphur existing in the mineral naturally, as it was expelled from its combination with iron, and also that any S, emitted by the fuel used in the process of calcination, has also been retained in a similar manner. Taking both these sources of sulphur into account, there would appear to be an unusual quantity of this substance present in the calcined ironstone, but I am not, on that account, disposed to question the accuracy of the statement, although there is, according to it, an apparent excess entering the furnace

This excess may be, and certainly to some extent is, accounted for by compounds of sulphur being carried off in the gases and fume; thus, in Section XXVII., the latter contained ·59 per cent. of SO_3, besides soluble alkaline salts, amounting to 3·07 per cent., in which, no doubt, S in some shape would be present. It is also pretty certain that the gases themselves will carry away some sulphur combinations, but in such a minute quantity as to be difficult to estimate. A very notable discrepancy between the two sides of the account will certainly arise from the SO_2, emitted by the slag during its passage from the furnace, the pungent fumes of which are easily recognised.

The difference in question, however, is comparatively unimpor-

tant for the object I have in view, which is to show that the S, unlike the phosphorus, is to be found chiefly in the slag, and to point out the precautions to be adopted in order to secure, as far as possible, its absence from the iron.

If silica is present in such quantity as when fused with alumina and lime, to form a perfectly vitreous slag, any sulphur is more or less expelled from the Ca, and is taken up by the iron. On the other hand, it would appear, when lime is in excess, there is a strong disposition for the S to be retained in the slag, possibly as Ca S. Now, fortunately, perhaps, for the quality of the iron obtained from the Cleveland ironstone, silica is deficient, and its office as an acid is, probably, partly discharged by alumina, so that the slags from the furnaces smelting this mineral may be regarded as silico-aluminates of lime, alumina, and magnesia. This composition permits the use of Ca O to such an extent that, when added to the lime naturally existing in the ore, it affords a cinder containing 40 per cent. and upwards of this earth.

To exhibit the difference in this respect between the slag run from a furnace in Cleveland, and that from other localities, the following analyses are given, in which the earthy compounds are stated in their relative proportions:—

	Ormesby. Exp. 614.	Clarence. Exp. 615.	Staffordshire. Exp. 616.	Dowlais. Exp. 617.
SiO_2	31	29	40	45
Al_2O_3 ...	23	25	15	13
Ca O	40	42	37	37
Mg O	6	4	8	5
	100	100	100	100

The numbers given below exhibit the amount of the four earths in the Cleveland ironstone, without any additional admixture of lime. Thus, in—

Cleveland ironstone from	Normanby Mines. Exp. 618.	Skelton Mines. Exp. 619	Average.
SiO_2	37	36	36·5
Al_2O_3	21	29	25·0
Ca O	28	22	25·
Mg O	14	13	13·5
	100	100	100·0

After satisfying myself that these proportions afforded a mixture quite as fusible as the slag ordinarily produced at the Clarence Works, I gradually withdrew from one of the furnaces the lime, until the burden of the furnace consisted of coke and ironstone only.

By analysis, the slag then gave the following numbers:—

Exp. 620.	$Si\ O_2$	35·95
	$Al_2\ O_3$...	25·55
	Ca O	23·05
	Mg O	9·00
	Fe O	1·45
	Mn O	3·15
	S	1·80
	P	tr.
	Ka_2 O and Na_2 O, by difference ...	·05
		100·0

In which we have the following proportions of—

$Si\ O_2$	38·5
$Al_2\ O_3$	27·4
Ca O	24·5
Mg O	9·6
	100·0

These figures, on adding the ash from the coke, will be found to correspond pretty closely with these earths found on other occasions in the ironstone.

Although the suppression of the limestone would reduce the quantity of matter to be fused by about 6 cwt. per ton of iron, the quality of the iron fell from grey to mottled, and the bar iron made therefrom was reported by Messrs. Hawks, Crawshay, & Sons to be of bad quality.

Exp. 621. The pig iron itself was found to contain

S, ·33 per cent.; and P, 1·58 per cent.

As a rule, I am inclined to think, the lower the temperature at which the furnace is working the richer is the iron in sulphur, and hence it will generally speaking be found that white iron, which is produced with least coke, or during an accidental derangement which

depresses the heat of the hearth, contains more sulphur than the grey iron, while no such difference attends the quantity of phosphorus present.

The following figures are extracted at random from several analyses of Clarence iron.

		S. per cent.	P. per cent.
Exp. 622	No. 1 Clarence.	trace	·30
„ 623	„ „ ...	·04	·30
„ 624	„ „ ...	·25	·30
„ 625	No. 3 „ ...	·04	·155
„ 626	„ „ ...	·10	·72
„ 627	„ „ ...	·17	1·23
„ 628	No. 4 „ ...	trace	1·00
„ 629	White „ ...	·342	1·434
„ 630	„ „ ...	·960	·26

In confirmation of the lower temperatures favouring the union of S with the iron, I may instance an observation made while experimenting on a process* suggested by myself a few years ago, by means of which it was attempted to recover the sulphur used in the manufacture of soda. This was done by fusing the soda waste with the oxide of iron left after the expulsion of the S from iron pyrites, and in this way a compound of S and Fe was obtained, to be used again as a source of sulphur.

While engaged in this manufacture it was noticed that whenever the temperature of the blast furnace, which was one 25 ft. high, and 10 ft. in the boshes, driven with hot air, rose above a certain point, white pig iron, instead of a sulphide, made its appearance. This was remarkable, seeing that the quantity of sulphur introduced into the furnace was sufficient to give, and frequently afforded, a sulphide of iron, containing 30 per cent. of sulphur.

Exp. 631. A specimen of this white iron contained 1·78 per cent. of sulphur.

The inference I would draw from the facts, given in the present section, is that with the actual mode of manufacture there appears little hope of being able to avoid nearly the whole of the phosphorus in the materials accumulating in the pig iron, but by the liberal use of lime, and by the maintenance of a pretty high temperature, nearly all the sulphur may be carried off in the slag.

* Described in Transactions of Chemical Society of Newcastle-on-Tyne.

SECTION XXXVI.—ON SOME OF THE CONDITIONS WHICH APPARENTLY AFFECT THE QUALITY OF THE IRON.

Unlike other metallurgical operations for obtaining a metal from its ores, the iron blast furnace delivers its product of different qualities, well known as foundry and forge iron. The former embraces the dark grey, in crystals, designated Nos. 1, 2, 3, and Foundry No. 4, the colour becoming lighter and the crystals smaller as we descend in the scale. Forge iron commences where the foundry ceases, and includes Forge No. 4, mottled and white. As is well known, however, to manufacturers, very grey iron is frequently used in the forge, and sometimes, for particular purposes, the forge qualities are required in the foundry. As a rule, a furnace is especially devoted at certain times to the production of a particular quality of metal, this being done by using a smaller quantity of ore, on a given weight of fuel, when foundry iron is sought for, than when forge iron is the object in view.

It may be inferred from this mode of treatment that, for the higher numbers, beginning at No. 1, a more intense temperature is necessary than for the lower, and in consequence of this greater heat, it is not unlikely there may also be some change in the chemical constitution of the product. As regards the first of these suppositions, there can be no doubt that a given quantity of fuel, having a reduced amount of duty imposed upon it, must perform that duty at a correspondingly increased temperature, and this view is confirmed by actual observation. With respect to the second, an opinion is prevalent that the "richer" the iron, as it is called, *i.e.*, the nearer it approaches to No. 1, the more carbon has it taken up, and the greater is the proportion of this carbon in the uncombined or graphitic state.

I propose to examine these two questions in the present section

I believe it will be generally admitted that if a furnace were working steadily with Cleveland stone, on rich foundry iron, say, half No. 1 and half No. 3, equal to average of No. 2, an addition of 1½ cwt. of mine to the burden carried by 1 ton of coke, would suffice to lower the quality to an average of No. 4, or about two numbers

below its former mark. This addition is equivalent to reducing the consumption of coke about ·8 cwt. per ton of iron. Assuming that in each case all the CO_2, generated by the action of the ore on the CO, escapes as such, this weight, ·8 cwt. of fuel, burnt with hot blast, will all escape as CO, and represent about 2,400 units. If this be correct, then each number, as we ascend in the scale, will require for its production, probably, about 1,200 units, or something like ·4 cwt. more coke than the number under it.

I was very anxious to determine, by actual experiment, the difference of temperature in a furnace while running different qualities of iron, and this I endeavoured to do by ascertaining the heat of the slag.

Several attempts were made to get this by introducing into an ordinary calorimeter, containing ice, a given weight of slag, as it ran from the furnace, and judging of the temperature by the quantity of ice which was melted. The numbers obtained were as follow :—

Exp. 632.	Ice melted per gramme of slag		... 7·01	grammes.
„ 633.	do.	do.	... 6·88	„
„ 634.	do.	do.	... 8·09	„
„ 635.	do.	do.	... 7·51	„
„ 636.	do.	do.	... 6·70	„
		Average	... 7·238	„

The variation is	from 6·70 × 79	calories	= 529	calories.
	to 8·09 × 79	„	= 639	„
	Average	...	584	„

The want of uniformity in these experiments, with the ice calorimeter, arising chiefly from a varying quantity of ice melting in the external chamber, induced me to try a different plan. A copper vessel, having a capacity of about 12 litres, was surrounded by an outer one, forming a hermetically closed air space. The whole was enclosed in a wooden case, to lessen the loss from radiation, &c. Ten litres of water of a known temperature were poured into the inner vessel, and kept in readiness close to the current of slag, the temperature of which had to be ascertained. A cast iron crucible, of a tapering form, capable of holding about 200 grammes

was placed in one of earthenware, to prevent loss of heat. A quantity of the slag was poured rapidly into the iron crucible, and a lid, luted with tempered clay, was pressed into it so as to exclude the water when the whole was immersed in the ten litres of water. As five minutes elapsed before the water ceased rising in temperature, experiments were made to determine the loss during this delay, which was ascertained to amount to 4·04 per cent.

The highest number obtained in this way was 504 calories per unit of slag, which is about 9 per cent. below that of M. Vathaire, possibly owing to loss of heat in transferring the slag to the crucible and the crucible to the water. Occasionally, the number was 40 calories below this, and this often, when the experiment was the most expeditiously performed, which induces me to think that, in the hearth of the furnace itself, there are irregularities of temperature, occasioned probably by changes in the quantity of fuel compared with the ore, arriving at the tuyeres. At any rate, the fluctuations were too great to render it easy to determine the difference in temperature of a furnace making different qualities of iron.

Exp. 637. At one of the Clarence furnaces, which had been working for some time steadily on No. 4 iron, the temperature of the blast was purposely lowered, so that something like 800 calories less per ton of iron entered the furnace. The iron fell to mottled and some white iron while the change was continued, but returned to No. 4, soon after raising the temperature of the air to its former pitch.

Being desirous of knowing whether the temperature of the escaping gases afforded any indication of what was going on in the hearth, two of the Clarence furnaces (capacity 25,500 cubic feet), and both working on the same burden of minerals, were experimented upon for periods of six to seven hours, upon different days. The temperatures were taken every ten minutes, by means of the electric pyrometer.

No. 4 furnace, making	No. 2 iron.	No. 3 iron.	No. 4 iron.
Temperature of gases	345°C.(653F.)	335°C.(635F.)	343°C.(650F.)
		334°C.(633F.)	
No. 5 furnace, making		363°C.(685F.)	347°C.(656F.)
		342°C.(648F.)	
		376°C.(709F.)	

From these figures which give 345°C. (653°F.) for No. 2 iron, an average of 350°C. (630°F.) for No. 3, and 345°C. (653°F.) for No. 4, it may be concluded that any excess of heat evolved during the production of the higher number was absorbed and carried away by the iron and slag, because there is practically no difference in the temperature of the escaping gases. In all probability, also, there would be somewhat less heat generated in making the lower quality of iron, most likely due to alterations in the quality of the coke itself.

Repeated allusion has been made, in previous portions of this work, to the complex nature of the action of the blast furnace, and how readily its progress is interfered with by irregularities in the quality of the materials, by want of care in charging, by alterations in the temperature of the blast, or even by changes in the atmosphere, and that these irregularities might amount to fully 5 per cent. on the fuel consumed, or even more. Nothing, therefore, is more easy to comprehend, than that a furnace making any given quality of iron, should slip down a number, or the reverse, when it is remembered that about one-fourth of this 5 per cent. suffices to cause the change.

As a rule, I have assumed, in my estimates of the standard of heat appropriation, that No. 3 iron was being produced, this quality, or from that to No. 3·5, being the usual average run from the furnaces in the vicinity of Middlesbrough.

I am aware my figures have been objected to by some of my fellow ironmasters, whose word is beyond dispute, and for whose experience and knowledge I entertain the highest respect. I believe these discrepancies may often, if not always, arise from a difference of the circumstances under which the furnaces are worked. Thus supposing a manufacturer required a large quantity of foundry iron, say Nos. 1 and 3, it would be necessary for him to work with such a burden as would ensure a margin of heat, which would cover all the contingencies I have mentioned, and even then he might receive as much No. 4 as would reduce the average to No. 3. On the other hand, a second maker holds orders chiefly for No. 4, and his furnaces are burdened accordingly, but owing to a combination of favourable conditions, he produces, over some days, nothing but No. 3 iron, which he, of course, will do with a consumption of fuel, which will contrast very favourably with that of his neighbour, who is bound

to furnish his customers with richer iron in the face of adverse conditions.

Before concluding this section, further proof will be adduced of the influence of temperature in determining the quality of iron from the blast furnace; but before giving this, it will be convenient to consider whether the application of this additional heat changes the chemical composition of the metal when it changes its quality in point of richness.

To determine this, a great number of analyses by the processes already described was made of iron of all numbers, of which the following are examples:—

Quality of the iron.	Exp. 638. Clarence No. 1.	Exp. 639. Clarence No. 1.	Exp. 640. Clarence No. 1.	Exp. 641. Clarence No. 3.
Fe, by difference...	92·913	92·288	92·601	92·550
P	1·502	1·174	1·338	1·570
S	·071	·055	·063	·108
Si...	1·683	1·585	1·634	1·372
C uncombined ...	2·282	2·722	2·502	2·758
C combined ...	·789	1·149	·969	·722
Slag	·760	1·027	·893	·920
	100·000	100·000	100·000	100·000
Total carbon ...	3·071	3·871	3·471	3·480

Quality of the iron.	Exp. 642. Clarence No. 4.	Exp. 643. Clarence No. 4.	Exp. 644. Clarence White.	Exp. 645. Clarence White.	Exp. 646 Wear White.
Fe, by difference...	93·003...	92·422...	93·181...	94·104...	90·908
P	1·480...	1·676...	1·318...	1·134...	1·554
S	·072...	·023...	·199...	·016...	·209
Si	1·531...	1·353...	·640...	·900...	2·025
C uncombined ...	2·504...	2·686...	2·209...	2·472...	2·539
C combined ...	·790...	·920...	·993...	1·014...	·745
Slag	·620...	·920...	1·460...	·360...	2·020
	100·000	100·000	100·000	100·000	100·000
Total carbon ...	3·294...	3·606...	3·202...	3·486...	3·284

If these figures are to be relied on, it cannot be pretended that carbon, either by greater quantity, or by any peculiarity of form, is the cause of the difference between white, and other kinds of iron; for there is to be found among the above, one case of No. 1 pig (Exp. 638) having 3·071 per cent., of which 2·282 is graphitic, against 3·284 per cent., of which 2·539 is graphitic (Exp. 646) in a sample of white iron. If, again, any other substance, found in the above specimens, is examined, it will be observed that there is no feature connected with its presence, to which we can ascribe the variations in quality.

The inference I would draw from the information afforded by these analyses is, that the condition of iron in respect to its so-called "richness" is, within certain limits, entirely independent of its chemical constitution. The assertion just made is not unreserved, because it is generally thought that an excess of sulphur greatly *hardens* iron, reducing it to the lower numbers, and ultimately converting it into "mottled," or even "white." The second inference to be drawn from what has preceded, is, that if the composition of the iron does not affect its quality, there is no alternative but to conclude that the change is due to alterations of temperature alone. Corroborative of this opinion is the well-known behaviour of iron, when suddenly cooled, by which even the richest iron, when run into a *chill*, becomes white; and, again, No. 1 iron, if run slowly from the blast furnace, may be reduced in physical appearance to No. 3.

It would appear, judging from the above analyses of Cleveland iron, that the metal, on being fused in the blast furnace, takes up a quantity of carbon, varying from a trifle above 3 to a trifle under 4 per cent., and that the actual quantity does not appear to exercise any influence in determining the nature of the product.

In the fluid state, I conceive the carbon, so taken up, confers upon the iron the property of fusion much below the temperature at which the pure metal melts, and the carbon itself may be regarded as dissolved in the iron. If, during the process of manufacture, the pig metal has been formed at a low temperature, consolidation, I imagine, takes place under such circumstances that the crystals are so minute, and the carbon which is separated assumes the uncombined or graphitic form in particles so minute as to be invisible, and in consequence, the iron is white. If, on the other

hand, the furnace is working at a very high temperature, the intensely heated iron crystallizes with large facets, upon which the extruded carbon assumes the condition of distinct plates or flakes.* Should the temperature be less intense, these crystals are of smaller dimensions, and the separated carbon is less conspicuous, and, as the temperature of the furnace declines, the crystals decrease in size, as do the flakes of carbon, until both disappear in white iron.

Exp. 647. I endeavoured to prove the correctness of this view by direct observation on the blast furnace itself. The immediate vicinity of the tuyeres is, of course, the focus of greatest heat, which diminishes rapidly in intensity at a very short distance higher up in the furnace. At a point about six feet above where the blast is admitted, the heat is one of very bright redness, almost white, and certainly quite enough to melt cast iron. I expected some of the iron would be fused at this locality, and, not having encountered the highest temperature of the hearth, would be white. A hole was drilled six feet above the tuyeres in the side of the Wear furnace; some pounds of fluid iron ran out, all of which was perfectly white, although the produce from the ordinary tapping hole, upon the occasion of the experiment, was foundry grey No. 3.

Anyone with the slightest acquaintance with an iron furnace is aware that if the burden of mine is raised beyond a certain point, the slag acquires a black colour, deepening in intensity as the excess of ore is increased. This is simply due to unreduced oxide of iron passing into the slag; and, being desirous of knowing whether the presence of a greater or less quantity of this oxide affected the quality of the iron, I had a number of analyses of slag made while the Clarence and Wear furnaces were working on known qualities of iron.

When running No. 1 iron, the slag contained of Fe per cent.:—

Exp. 648.	Exp. 649.	Exp. 650.	Exp. 651.	Exp. 652.	Exp. 653.	Exp. 654.	Average.
·71	1·06	·89	·44	·28	·27	·52	·59

When running No. 3 iron, the slag contained of Fe per cent.:—

Exp. 655	Exp. 666.	Average.
·84	·33	·58

* A very interesting paper, on the occurrence of graphite in cast iron, was read by Mr. G. J. Snelus, of Dowlais. In it, the author states that, by mere mechanical means, a considerable quantity of carbon in this form was separated from the iron.—*Vide* Journal of Iron and Steel Institute.

When running No. 4 iron, the slag contained of Fe per cent.:—

Exp. 667.	Exp. 668.	Exp. 669.	Exp. 670.	Exp. 671.	Exp. 672.	Exp. 673.	Average.
·54	·47	·69	·58	·47	·81	1·00	·65

There is obviously nothing in these numbers to connect the nature of the product with the quantity of iron in the slag.

Returning, then, to temperature as the cause of differences in quality of pig iron, the "chilling" of grey metal, and its conversion into white, may be regarded as the effect of preventing, by rapid cooling, the formation of crystals sufficient in size to render their coating of carbon visible.

If a quantity of this white iron is introduced in a cupola, as soon as it is heated to its melting point, it fuses, and runs to the bottom of the furnace. On being run out, it solidifies under conditions even less favourable for visible carbon separation than when it was produced in the blast furnace; inasmuch as the temperature of a cupola is below that employed for smelting iron. As might be expected, the iron is still white, at all events when run into masses of moderate size.

If, however, such dimensions are given to the fused mass as to produce very slow cooling, then, in spite of the comparative lowness of temperature, the crystals assume a size which permits separation of carbon in a visible form, and in consequence the iron becomes more or less grey in colour.

To prove this, I had a mould made, being a cube of 3 feet, and, therefore, capable of holding five or six tons of metal. The mould was dried and warmed, and into it was run this quantity of white iron. The whole was then covered up with sand to retain the heat as long as possible. At the end of some days the iron was removed, and by means of a heavy weight falling on a steel wedge placed in a cavity cast to receive it, the block, with one blow, was split through the middle.

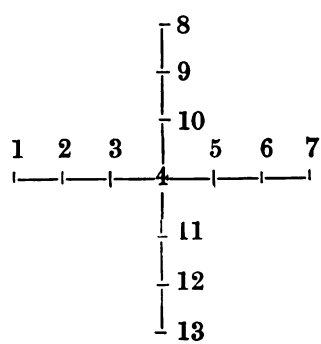
The edges of this fractured surface were white, with a few circular patches of grey; these increased as the centre was approached, and, at a distance of two or three inches from the outside, the colour was grey interspersed with patches of white, so that at a little distance it resembled grey granite. One *git* or pouring place, which fed from the bottom upwards, was grey forge at its lower end. Another *git*, which filled an orifice made to permit the air to escape from the top of the mould, was entirely white.

The following four samples were then analysed:—

	Exp. 674. Original pig.	Exp. 675. White git.	Exp. 676. Grey git.	Exp. 677. Near centre of block. mottled.
Uncombined carbon	2·209	2·198	2·472	2·296
Combined „	·993	·666	1·014	·644
Phosphorus	1·318	1·344	1·134	1·346
Sulphur	·199	·197	·016	·007
Silicon	·640	·860	·900	·760
Slag	1·460	1·020	·360	·920
Iron by difference	93·181	93·715	94·104	94·027
	100·000	100·000	100·000	100·000
Iron by analysis	92·650	94·250	93·850	94·500
Total carbon	3·202	2·864	3·486	2·940

The chief alteration appears to be, that remelting has removed more or less of the slag. The phosphorus remains the same; the silicon has increased; and the sulphur, in the grey and mottled iron, has notably diminished. The carbon is lessened in two of the cases, and increased in the third.

To ascertain whether the decrease of sulphur in Exp. 676 and 677 was not merely accidental, the block had two lines drawn at right angles across the centre of the fractured face, and specimens were drilled out at intervals of 6 inches, and numbered thus:—



Of these, a certain number were analysed and gave the following results:—

	Exp. 678.	Exp. 679.	Exp. 680.	Exp. 681.	Exp. 682.	Exp. 683.	Exp. 684.	Exp. 685.	Exp. 686.	Exp. 687.
Per cent.	No. 1.	No. 2.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.	No. 11.	No. 13.
S	·234	·218	·195	·234	·236	·248	·242	·234	·200	·242
C comb.	--	—	·626	·720	·626	·770	—	—	—	—
,, uncomb.	--	—	2·046	2·008	3·132	2·236	—	—	—	—
Total C	2·842	2·978	2·672	2·728	2·738	3·006	2·802	2·776	2·788	3·070

The foregoing experiments were undertaken partly to see whether, as with the Ag and Pb in the case of the Pattinson process of desilverizing lead, any combinations of Fe and those substances which are associated with it in pig iron, remaining liquid longer than others, might be found to be concentrated in particular portions of the mass.

From these numbers we may regard the whole block as possessing a uniform composition as regards sulphur and carbon.

In order to secure the exposure of some white pig iron to a temperature which was known to suffice for the production of grey, the following trial was made :—

Exp. 688. A furnace running No. 3 iron was selected, and at a point a few feet from the opening where the slag flowed out, a channel and a basin in its course was scooped out in sand, so that when the slag ran down the channel the small reservoir contained a certain quantity in a fluid state. The current was continued long enough to prevent the cold sand materially affecting the temperature of the molten mass, which as usual ran through an external crust. Quite close to where the stream left the furnace, and, therefore, before it had parted with any notable quantity of heat, a bar of white iron was inserted in the current, where it speedily melted, and as the globules of metal dropped off the bar they were carried forward by the slag down the channel until they were intercepted by, and retained in, the basin. In this way they were exposed to heat closely approaching that of the interior of the furnace itself. When a few pounds were thus carried off, the current was diverted and the iron removed when solid, and found to be No. 3, although not above one inch in thickness.

Exp. 689. A quantity of the iron obtained in the previous experiment was melted in a crucible, and run into a mould having a transverse sectional area of about one inch, to see whether there was any tendency to re-assume the condition of white iron. It

remained perfectly grey, but became closer in the grain, not more so, however, than a specimen of ordinary No. 3 iron, when treated in a similar way.

What the temperature to which this iron was subjected is I have been unable to determine. One step towards this would have been ascertaining accurately the quantity of heat contained in the liquid contents of the furnace. In this, as has been stated, I have hitherto failed; but were we in possession of the necessary information, the absence of all data as to the specific heats of bodies at very high temperatures prevents further progress in the estimate.

Exp. 690. The only experiment I performed in the direction indicated, consisted in immersing a piece of bar iron in the slag runner in the manner observed with the white pig iron, the produce of the furnace itself at the time being grey No. 3. It was fused and collected in the basin, still preserving the property of malleability. The melting point of this substance is stated by Daniell to be above 1,800°C. (3,272°F).*

Karsten determined that grey iron had a higher melting point than white iron, and mentions that this latter variety might be converted into grey iron by very slow solidification at a high temperature, as well as that grey iron became white on sudden solidification. Dr. Percy† questions the conversion of white into grey iron, under the circumstances described, as a universal law; but I imagine this difference of opinion may be due to proper precautions as to slowness of cooling not having been observed. So far as my own recollection serves me, this change from grey to white, and a partial change at all events of white to grey (mottled), are facts which were well known to every practical ironfounder long before the date of Karsten's paper containing the opinions quoted above, which was written in 1846.

Gurlt, from reasons founded upon certain supposed definite compounds of iron and combined carbon, conceives greyness and whiteness in iron to be determined by their respective compositions, and mottled to be a mixture of the two. In support of this, he speaks of having converted spiegeleisen containing manganese into grey iron by simple exposure to a temperature much higher than its own melting point. What the nature of the change, if any, may

* Daguin (Traité de Physique) gives 1,500 degs. C. as the fusion point of *fer doux*, and 1,600 degs. C. as that of *fer écroui*, apparently on the authority of Pouillet.

† Percy's Metallurgy, Iron and Steel, p. 112.

be when the metal is fluid probably no one can say, but so far as its composition after solidification is concerned it would be difficult to ascribe any change in its physical aspect to any alteration either in its content of carbon or in its chemical constitution. This at least is what may be gathered from the analyses of the pig iron used for the large block described in this section, the different portions of which were stated to contain—

Exp.		Uncombined Carbon.	Combined Carbon.	Total.
674.	White pig iron, before fusion, per cent.	2·209	·993	3·202
675.	White git after fusion	2·198	·666	2·864
676.	Grey do. do.	2·472	1·014	3·486
677.	Centre of block do., mottled	2·296	·644	2·940
680.	Do. do., do.	2·046	·626	2·672
681.	Specimen 6 inches from centre, mottled	2·008	·720	2·728
682.	Do. 6 „ from outside, do.	2·132	·626	2·758
683.	Do. next outside, nearly white	2·236	·770	3·006

According to Gurlt, says Dr. Percy, grey iron is an octocarbide intermingled with graphite and white iron a tetracarbide. The latter is formed at a low heat, comparatively, and is resolved at a higher temperature into octocarbide and graphite. The Doctor commends Gurlt's theory for its simplicity, but objects to the conclusion which practically makes difference of temperature explain everything.

Unless the numbers indicating the total quantity of carbon in my large cube, as well as those denoting the weight of this ingredient in its so-called combined and uncombined condition, involve a good deal of experimental error, I am disposed to agree with Dr. Percy that it is improbable that the production of one kind of iron depends on the decomposition by temperature of another; but I do feel inclined to adopt the conclusion this author hesitates to consider as founded on truth, viz., that difference of temperature may, and probably does, explain everything.

On the other hand, Karsten, and after him, Janoyer and Percy, appear to have proved that sulphur expels carbon from iron at a high temperature. I have not myself made this question the subject of examination, but I may state it as a matter of belief among practical men that sulphurous coke in the blast furnace,

and the use of this kind of fuel in the foundry cupola, so hardens the iron that it is apt to be white towards the edges.

Pig iron, although always containing other matter than iron and carbon, consists essentially of these two elements alone, inasmuch as if perfectly pure $Fe_2 O_3$ is heated with pure C, a substance analagous in character to pig iron is obtained.

The composition of the crude or pig iron of commerce differs, however, considerably from the substance produced under such conditions as those just described, and as the elements other than those previously named, and which may be regarded as impurities, are of course derived from the minerals used, the extent of such contamination will in a great measure depend on the quality of the fuel, ores, and flux employed in the blast furnace.

Although the substances which enter a blast furnace may be, and are, very numerous, it by no means follows that they of necessity find their way into the pig iron. What the circumstances are which determine the absorption of varying quantities of some of them by the metal our knowledge of the process is at present too limited to pronounce.

Phosphorus, under all circumstances, as we have seen in the previous section, may be assumed as being almost entirely taken up by the iron; whereas sulphur, by the copious use of lime and a high temperature, is almost as completely found in the slag.

Manganese, when a constituent of the ore, is found partly in the iron and partly in the slag. Upon one occasion* when using an admixture of a manganiferous ore, containing 30 per cent. Mn and 17 per cent. Fe, with the Cleveland stone, I found the different qualities of iron contained

	No. 1 Pig.	No. 2 Pig.	No. 3 Pig.
Manganese	1·75	2·31	2·45
Carbon	2·94	2·90	3·30
Sulphur	·292	·247	·254
Phosphorus	·416	·860	·867

The slag produced at the time of the addition of this manganiferous ore contained—

* Report to British Association, 1863, I. L. Bell.

Si	29·25
$Al_2 O_3$	19·25
Ca O	38·25
Mg O	·60
Fe O	1·04
Mn O	8·76
Si	2·16
$Ti O_2$	·75
	100·06

By calculation, it appeared of 100 parts of manganese which entered the furnace, there was

United with the iron	9·5
Found in the slag	87·6
Unaccounted for	2·9
	100

Of the other foreign ingredients the only one of importance, either from its almost universal presence in, or its effect on, the iron, is silicon.

In the analyses quoted in the present section it will be observed Si varies considerably in quantity in the iron smelted from Cleveland stone. It has been pretended that this substance is an essential ingredient in pig iron, but looking at some analyses, and at the fact that cast iron may be produced from carbon and pure iron, there seem no good grounds for the assumption.

With regard to the influence of Si on the quality of pig iron, it may be questioned whether it is ever beneficial. Even in moderate quantities the metal itself is undoubtedly rendered weak as a material for the purposes of the founders, and its presence in any quantity in forge iron is undoubtedly detrimental, inasmuch as it not only yields no malleable iron, but, on the contrary, it carries off a large quantity of Fe as a silicate.

From this somewhat general condemnation, I understand, must be excepted a moderate amount of Si in iron destined for the production of Bessemer steel. Here the heat evolved by the generation of SiO_2 is regarded as helping the process, and may also possibly

assist in forming a vehicle by means of which some of the other impurities are removed from the product sought for.

Under these circumstances, viz., that the presence of Si at one time and its absence at another are desirable, it becomes a subject of some interest to enquire what are the conditions which are most conducive to the reduction of SiO_2 and the absorption of its base by the iron.

With the exception of Exp. 646, in which Si appears in excessive quantity in a specimen of white iron, its presence is promoted by a high temperature which is, as might be expected, favourable to the decomposition of SiO_2, because, as a rule, the "richer" the iron the more Si is there in the pig, and we have seen "richness" is acquired at the expense of heat. Thus the percentage of Si is in—

making No. 1.	making No. 3.	making No. 4.	making white.
Exp. 638. 1·683	Exp. 641. 1·372	Exp. 642. 1·531	Exp. 644. ·640
„ 639. 1·585		„ 643. 1·352	„ 645. ·900
„ 640. 1·634			
Average 1·634	1·372	1·421	·770

There occurs, however, occasionally, at most ironworks, a state of things which leads to the production of a kind of iron known, in the North of England, under the name of "glazy metal." This variety of pig is grey in the fracture, somewhat leaden in its aspect, and is composed of small crystals. With these peculiarities well marked, it is scarcely too much to say, the article is almost entirely worthless. In castings, it is weak to rottenness, and in the puddling furnace it melts like water, and so completely defies the exertion of the puddler, that his "fettling" disappears long before the obstinate material he is operating on shows any signs of "coming to nature."

I have known a furnace go upon this quality of iron, and, before its condition came to my knowledge, make a couple of hundred tons of this valueless substance. The cause of its appearance is generally considered to be dependent on excessive heat in the furnace, at all events, raising the burden of the ore, or lowering the temperature of the blast, which latter has the advantage of being a readier mode of cure, always puts an end to its production.

Two specimens of glazy iron were analysed, and found to contain*—

Fe	88·18 ...	90·70
C combined ...	·79 ...	·71
C uncombined ...	2·59 ...	2·68
Si	5·13 ...	5·13
Mn...	·77 ...	·56
S	·17 ...	·23
P	1·12 ...	1·12
Ti	·26 ...	·18
Ca	·22 ...	·20
Mg	·06 ...	·03
	99·29	101·54

From what has preceded, it seems within our reach to avoid deteriorating the quality of our iron by an excessive amount of Si, by avoiding too high a temperature; but, on the other hand, as the "richer" kinds of iron are dependent for their production on the application of more intense heat than the lower numbers, the same cause which gives us "rich" iron may increase its content of Si, and hence the difficulty of our altogether avoiding the presence of this substance. This is particularly the case in Cleveland iron, which, from what I consider the comparative infusibility of the slag which accompanies its production, requires, in my opinion, a somewhat higher temperature than that demanded in the treatment of more silicious ores. A portion of the silica exists in its combined form in the ore, and this also may promote the readiness with which this constituent is decomposed, and thus account for the somewhat excessive quantity of Si in the pig iron made in the district in question.

* I. L. Bell: Report to British Association, 1863.

SECTION XXXVII.—ON SOME OF THE MODIFICATIONS OF THE ACTION OF THE BLAST FURNACE, ARISING FROM CHANGES IN ITS DIMENSIONS.

The known influence which foreign matter, in almost infinitesimal quantities, exercises on the quality of pig iron, suggested the enquiry whether, when the furnaces in which the operation of smelting was performed were greatly increased in size, some change in the composition of the product might not have accompanied the alteration in the apparatus.

As a matter of general opinion, I may state, that in late years, the pig iron obtained from the ore of the Cleveland hills has risen in public estimation; but whether this is due to any peculiarities it may possess being better understood, or to any actual improvement in its quality, would be difficult to say.

For some time before and after the introduction of large furnaces, a series of monthly trials was made at the Clarence Works, to obtain, if possible, some information respecting the comparative strengths of iron made in furnaces of different sizes. On the whole, the results were favourable to those bars run from metal smelted in the larger furnaces, but, occasionally, the experiments gave, as generally happens upon similar occasions, somewhat contradictory numbers.

Each month, half a dozen specimens from each furnace were tested, and the average taken. Of course, in all cases, the size of the bars and the distance between the supports were the same.

	Exp. 691.	Exp. 692.	Exp. 693.	Exp. 694.
Furnace of	6,000 c. ft.	11,500 c. ft.	15,500 c. ft.	25,500 c. ft.
Trials extending over	4 mths.	3 mths.	12 mths.	13 mths.
	Cwts	Cwts.	Cwts.	Cwts.
Minimum breaking weight ...	26·5	26·2	24·0	23·6
Maximum do. ...	27·6	28·2	30·5	31·2
Average	26·8	27·2	28·2	27·5

Independently, however, of any improvement, in a commercial point of view, which had followed the enlargement of the furnaces, it cannot be otherwise than interesting, and it may be important, to examine, by means of actual analysis, whether the prolonged expo-

sure of the ore to the reducing agency of the furnace, accompanied by prolonged contact with the injurious ingredients it meets with during its descent to the hearth, have affected in any way the composition of the pig iron.

The only chance we possess of determining this, is by comparing the analyses of specimens of iron made in different sized furnaces.

Composition of Iron smelted in Furnaces containing under 6,500 *cubic feet—*

	Exp. 695. Clarence No. 1 iron. Average 3 Samples.	Exp. 696. "Tees," "Clev.," and S. Bank. No. 1 iron. Average. 3 Samples.	Exp. 697. Clarence No. 3 iron. Average 3 Samples.	Exp. 698. Clarence No. 4 iron. Average 2 Samples.
C combined ...	·73	·41	·65	·76
C uncombined ...	2·53	3·03	2·16	1·76
S	·13	·14	·10	·40
P	·30	1·24	1·16	1·28
Si } Slag }	2·53	2·39	1·76	1·86
Fe, &c., by difference	93·78	92·79	94·17	93·94
	100·00	100·00	100·00	100·00
Total carbon ...	3·26	3·44	2·81	2·52

Composition of Iron smelted in large Furnaces, containing 11,500 *cubic feet and upwards—*

Quality of iron :—	Exp. 699. Clarence No. 1.	Exp. 700. Clarence No. 3.	Exp. 701. Clarence No. 4. Av. 2 Samples.	Exp. 702. Wear No. 4.
C combined ...	·969	·722	·855	·745
C uncombined ...	2·502	2·758	2·595	2·552
S	·063	0·108	·047	·169
P	1·338	1·570	1·578	1·502
Si	1·634	1·372	1·442	1·290
Slag	·893	·920	·770	·897
Fe, &c., by difference	92·601	92·550	92·713	92·845
	100·000	100·000	100·000	100·000
Total carbon ...	3·471	3·480	3·450	3·297

Average of the above eight Analyses—

	Iron from small furnaces.	Iron from large furnaces.
C combined ...	·64	.823
C uncombined ...	2·37	2·601
S	·19	·096
P	1·00	1·497
Si and slag ...	2·13	2·305
Fe, &c., by difference	93·67	92·678
	100·000	100·000
Total carbon ...	3·01	3·424

I do not consider that it would be safe to accept all the differences exhibited in these figures as conveying a true state of the case. Thus the iron from the lesser furnaces is in all probability understated as regards its phosphorus, the smallness of the weight of this ingredient being most likely due to the means of analysis being, at that time, less perfect than those recently adopted. This objection, however, does not apply to the content of carbon, and this substance, in both its combined and uncombined forms, appears in larger quantity in the iron smelted in the larger furnaces.

My wish, however, in the present section, is to draw attention to some other modifications than those of chemical composition of the iron, which modifications, I conceive, are influenced by the dimensions of the furnace. These have chiefly reference to the gradual changes effected upon the materials under treatment during their passage from the throat to the hearth. To some extent this subject, as I propose treating it, has been already dealt with in those sections which were devoted to considering the sources of heat, and in that (Section XXXIV.) which spoke of the changes experienced by the contents of the blast furnace. At the risk of occasional repetition, I will venture to dwell for a short time upon the questions which necessarily arise when these two branches of the enquiry are viewed in connection with each other.

To assist in this, diagrams have been prepared, in the hope that, by means thereof, I shall be able more clearly to explain my meaning. The horizontal divisions in the ruled paper represent the height of the furnace in feet. In the shaded portion of the figures the vertical lines show relatively the quantity of heat units

contributed by the three sources of heat, each square being roughly equivalent to 2,000 units. The central and lightest shaded space is intended to exhibit the heat of the blast, and the two spaces on the outside of it are intended for the heat units derived from the coke burnt to CO. The inverted triangular space at the top shows, by the position of its apex, where the heat commences to be developed by the conversion of a portion of the CO to CO_2 by the action of the ore; and the length of the base line indicates the quantity of heat so generated. The two strong black lines which run in a curved direction through the shaded portion of the diagram are laid down with the view of showing, by their flexure, the temperature of the interior at different points of its altitude.

The data upon which the curve itself has been constructed were obtained in the upper portion from direct observations made by means of Siemens's electric pyrometers. In the lower portion, where the temperatures are beyond the range of these instruments, the intensity of the heat was judged as nearly as the eye could do it by the state of incandescence of the contents, or by the behaviour of metals when exposed to its influence.

The quantity and intensity of the heat in the hearth is intended to be represented by the length of the line *A B* (Fig. 1). This heat is derived partly from the action of the hot blast upon the carbon it meets at the tuyeres, and partly from the following cause. The solid materials filling the hearth become intensely heated by the active combustion which prevails in that region. But the gaseous contents acquire the same temperature as the solid, and the former, having a weight of about one and a-half times that of the latter, rush with immense velocity towards the higher part of the furnace. Under these conditions, it is evident a vast quantity of heat must be carried along with the highly-heated gases by this rapid journey upwards. The effect of this current of hot gaseous matter on the solid contents travelling in an opposite direction is an equalization of temperature, *i.e.*, the ore, coke, and flux become heated at the expense of the gases, and, charged with this absorbed heat, they arrive at the tuyeres, where the heat, proceeding from combustion of the fuel added to that contained in the solids, gives the quantity and intensity represented by the length of the line *A B*.

To obtain an idea of the extent of the magazine of heat stored up in a large furnace by this process of interception, the following estimate has been compiled, based on the observations which are given along with the calculation itself.

Exp. 703. An average weight per cubic foot of the materials, as they are filled into the charging barrows, was ascertained to be as follows:—

Coke	·218 cwt.
Limestone	·678 „
Calcined ironstone ...	·607 „

A new furnace of 25,500 cubic feet was filled, before the blast was laid on, with the following materials, which, according to the above weights, would occupy the spaces annexed to each.

Coke ...	204·12 tons	at	·218 cwt.	per c. ft.	=	18,712 c. ft.
Limestone	64·72 „		·678 „	„	=	1,935 „
Calcd.ironst.	188·00 „		·607 „	„	=	6,194 „
						26,841 „

The resemblance between the actual capacity of the furnace, and the cubic feet of materials required to fill it proves their estimated weights to have been fairly correct.

The blast was now laid on, and there was charged into the top in 96 hours—

					Cubic feet.
Coke ...	153 tons	= at	·218 cwt.	per cubic ft.	... 14,037
Limestone	76 „	= „	·678 „	„	... 2,242
Ironstone	278 „	= „	·607 „	„	... 9,160
					25,439

A third measured quantity was introduced during the succeeding 96 hours—

				Cubic feet.
Coke ...	158 tons	... at ·218 =	cubic feet	... 14,495
Limestone	78 „	... „ ·678 =	„	... 2,302
Ironstone	300 „	... „ ·607 =	„	... 9,844
				26,641

We have, therefore, in these three measured quantities, as nearly as can be, the furnace filled three times.

A record was kept of the temperature of the gases, from which was estimated the heat they contained, and to it was added the heat absorbed for the quantity of iron made. On the other hand, by estimating the heat evolved by the combustion of the coke consumed, the actual number of heat units retained by the furnace was obtained.

First period:—

					Heat units.
Carbon burnt in hearth to CO					
Weight of coke ...	4,080 cwts.				
Less weight of ash and C carried off by CO_2 of flux	460 „				
	3,620 „	× 2,400	=		8,688,000
Of this C as CO will be burnt to CO_2, say ...	487 „	× 5,600	=		2,727,200
Blast required, heated to ... 412°C ...	20,983 „	× 412 × ·237	=		2,048,864
					13,464,064

The average temperature of the gases on the four days during which the above quantity of materials passed through the furnace was as follows:—

1st day.	2nd day.	3rd day.	4th day.	Average.
280°F.	290°F.	405°F.	516°F.	372°F.

The weight of gases was estimated at 25,208 cwts.; hence 25,208 cwts. × 189°C. × ·24 SH= 1,141,922

The iron made from 188 tons ironstone would be about 77 tons, requiring, exclusive of heat in the gases, about 84,600 heat units per ton 77 × 84,600* 6,514,200

7,656,122

Retained in furnace, end of first period ... 5,807,942

Vide Table Section XXIX.

Second period:—

Carbon burnt in hearth to CO—

			Cwt. ht. units.
Weight of coke ...	3,060 cwts.		
Less weight of ash and C carried off by CO_2 of flux	410 „		
	2,650 × 2,400 = ...	...	6,360,000
Of this C, as CO, there will be burnt to CO_2 747 cwts. × 5,600 = ...		...	4,183,200
Blast ... 15,360 cwts. × 412°C. × ·237 S.H.		...	1,499,700
			12,043,900

Weight of gases ... 18,780 cwts.

Temperature.						
1st day.	2nd day.	3rd day.	4th day.	Average.		
673°F.	680°F.	680°F.	690°F.	680°F.		
18,780 cwts. × 360°C. × ·24 SH =					...	1,622,592
Iron made, 117·5 tons × 84,600 =					...	9,940,500
						11,563,092
Retained in the furnace						480,808

Thus it was not until the fifth day after blowing in, that the gases approached the temperature at which they usually flow off from such a furnace, and consequently it will be perceived that during the second period which commenced with this day, almost the whole of the heat evolved was accounted for by the iron made, and by that which escaped with the gases.

The account as it stands leaves

5,807,942 + 480,808 = 6,288,750 cwt. heat units

as having been stored up, a small part in the brickwork, but chiefly in the quantity of materials which entered the furnace during the *third period*, of which 153 tons was coke.

In round numbers, this coke will produce, by its combustion, 9 million cwt. heat units, but the temperature will be raised in intensity by the addition of above 6 million units, which have been absorbed by the materials, resulting from the fuel which was burnt during the *period* which preceded it, so that practically it may be taken that the heat actually being evolved at any given period contains in its sum about 70 per cent. of that previously generated and intercepted by the current of solid matter down the furnace.

These figures speak forcibly on the value of a sufficiently high

column of materials, which has to catch and retain a quantity of heat, represented by fully 150 tons of coke, and it is obviously the absence of this store of caloric, which, when a furnace is first blown in, even with a very light burden of ironstone, always gives "poor" iron for the first cast or two. It is a well known law in physics that equalization of temperature takes place most rapidly between bodies when the differences of temperature are the greatest. It is partly owing to this law, and partly owing also to the heat which, from the nature of the operation, accumulates during the downward progress of the ore, &c., that the lines representing intensity curve so rapidly immediately after they leave the hearth, showing by their flexure a rapid fall in the temperature of the interior of the furnace.

It is this law, too, which indicates that the proper shape of the furnace is an inverted cone, in the diminishing area of which, when the communication of heat is the most rapid, the motion of the substances to be heated may also be the quickest, and as this rapidity of communication of heat falls off, the solids travel more slowly through the expanded area of the upper portion of the interior.

As we approach the summit, it will be seen that the dark curved lines approach more and more to the perpendicular, and therefore to the parallel, which proves how inefficient even a very large addition to the capacity of a furnace must be in intercepting heat contained in the gases, when this has to be done by means of substances between which and the gases themselves there no longer exists any very great difference in temperature.

It will be perceived that for some feet previously to arriving at the apex of the triangle, there has been but little change in the internal heat. This level is about the point where (the analyses given in Section XXXIV. show) we first meet with oxygen obtained from the reduction of the ore. The heat consequent upon the union of the oxygen with CO is very great, being, in the case of an 80-feet furnace, nearly 40 per cent. of the total amount evolved. All this heat (40 per cent.) is generated in the last 12 feet, in the case under consideration, and indeed the greater part is evolved much nearer to the top than even this; but, inasmuch as nearly the whole is at once absorbed by the process of reduction itself, this operation and the cold coke, limestone, and earthy constituents of the ore suffice to continue cooling the gases at even a

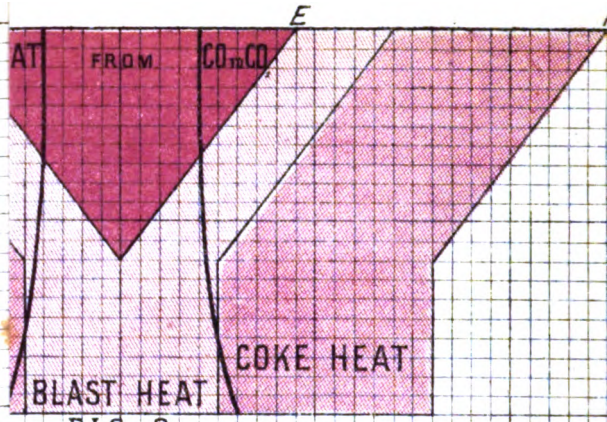
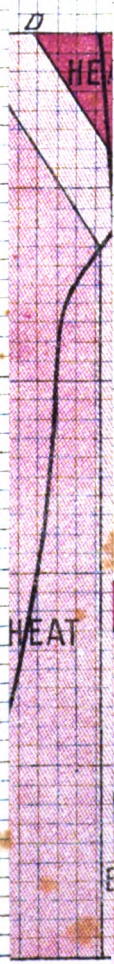

E
F
AT FROM CO TO CO
COKE HEAT
BLAST HEAT

FIG. 2


D
HEAT

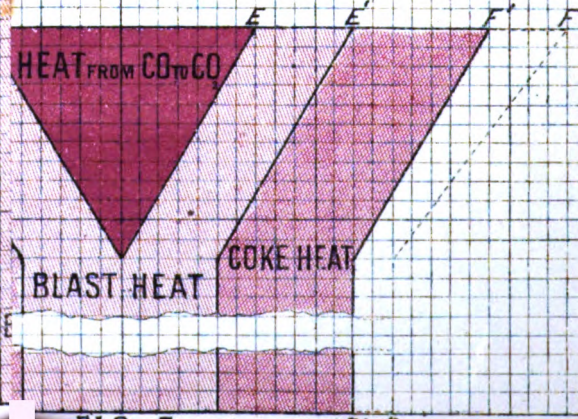

E
E'
F'
F
HEAT FROM CO TO CO
BLAST HEAT
COKE HEAT
B' B

FIG. 3

somewhat quicker rate, judging by the curve, than happened before they entered the zone of reduction.

In the diagram (Fig. 1), the small quantity of CO_2 in the gases along with the quantity of C and O, are accepted as an indication that reduction is completed before the iron oxide has arrived at this point, which it would do, at the ordinary rate of driving, in about 12 hours. The composition of the gases, at the period of their escape, also shows that the full quantity of CO_2, which is due to the action of the CO on the ore, is present; and hence, that there has been no loss by CO_2, generated by deoxidation of $Fe_2 O_3$, dissolving C, which action would be attended with a loss of 3,200 units for every unit of carbon so carried away.

The small quantity of CO_2 alluded to, as found in the gases at a depth below the 12 feet,* never amounts to that contained in the limestone: it may, therefore, be assumed that it is a portion of the CO_2 which is liberated from Ca CO_3, when the temperature is insufficient for its immediate reduction to CO by the heated carbon it meets.

A furnace, working in the manner represented by the diagram,† Fig. 1, may be considered to be doing so as efficiently as the nature of the ore (Cleveland) will permit. The height of the column, through which the heated gases are flowing, is sufficient to have enabled them to transfer all the sensible heat they are capable of surrendering, to the in-coming materials. Practically, this is done, perhaps, even more perfectly than the direction of the curved lines would indicate, because it must be remembered that the gases are approaching, at a distance of 65 to 70 feet from the hearth, a region where the combustion of CO into CO_2 checks their further cooling. That the supposition of 80 feet sufficing for intercepting all the heat which can be obtained from the gases is correct, has been demonstrated by the fact of the Eston furnaces, 95 feet high, passing off theirs no cooler than those at the Clarence Works.

The next limit to further diminution in the quantity of fuel is the composition of the gases. In Fig. 1, the sum of the length of the lines *C D, E F* represents the heat due by the action of the hot air on the coke and *D E*, that of CO to CO_2, and I am assuming that in

*Section XXXIV.

†The diagrams are constructed as if the materials occupied a height of 80 feet, whereas in reality, owing to the space required for the cup and cone, it would be a few feet short of this.

these proportions, and at the temperature represented by the distance at which the two curved lines are apart, all further action on Cleveland ore ceases.

I propose, hereafter, going at some length into considering the *minimum* of fuel which can be used to produce a ton of iron; but, with the diagram before us, it will be convenient to consider, at present, what the effect would be, in respect to economizing combustible, of altering the lengths of the lines *C D*, *E F*, say, by adding to that portion of them represented by the hot air, as is shown in Fig. 2.

The length of *C D*, *E F* is now extended by as much as the breadth of the space intended for the blast heat, *D E*, is widened.

If the addition to the temperature of the blast were only slight, then, it is possible, the only alteration would be a rise in the heat of the escaping gases, which is noted by an increased distance of the strong, black, curved lines from each other in Fig. 2. In Fig. 1, the space embraced by the triangle has such a temperature that the tendency of CO to rob $Fe_2 O_3$, or a lower oxide of iron ($Fe_x O_y$), of their oxygen is greater than that of the resulting CO_2 to dissolve C, and, in consequence, the latter tendency is held in check.

It is more probable, however, a change of a different character would take place, viz., a diminution of the line *D E* in Fig. 2, by as much as *C D* and *E F* had been lengthened, because it has been assumed in Fig. 1 that the space included within the triangle had such a temperature that the tendency of CO to deprive $Fe_2 O_3$, or lower oxides of iron of their oxygen is greater than that of the resulting CO_2 to dissolve C, and, in consequence, this latter action is held in abeyance. If the temperature of the space in question is raised, which it would be, in common with the rest of the furnace, by an addition to the heat of the air, this position of equilibrium would be disturbed by the activity of CO_2 to dissolve C becoming intensified. CO_2 would disappear, and the temperature of the escaping gases would fall to their original point by the cooling operation of this change in their chemical composition.

Of course, the mere addition of heat to the blast would, of itself, be productive of no economy unless the coke were at the same time decreased in quantity, and I propose to exhibit more fully the effect of this disappearance of CO_2 by the diagram Fig. 3, in which the total amount of heat, afforded by the blast and the coke, is the

same as that in Fig. 1, *i.e.*, *C' D'*, *E' F'* (coke heat) are shortened as much as *D' D*, *E E'* are lengthened.

The heat, then, under these altered conditions is supposed to be precisely in quantity and intensity what it was before the change, for that which has been suppressed as contributed by the coke has been made up by additional heat units in the blast. But this diminution of coke means diminution of CO, and hence when a fresh charge of ironstone is introduced, after the change in the composition of the heat, CO_2 is formed as before, but it stops in respect of deoxidation as soon as it amounts in quantity to that sufficient to form a neutral atmosphere with the reduced quantity of CO now present. The ironstone, however, of course, continues to descend, and ultimately surrenders the whole of its oxygen, but it is only able to do this by the newly formed CO_2 setting up a new condition of equilibrium, which it effects by acting on the heated carbon it meets, and generating such a quantity of CO as to be able to continue along with the original CO in the gases—the process of reduction. The evil, however, is only fully felt when the charges which have been deoxidized by the gases deficient in carbon to the extent of that represented by the coke which has been suppressed, arrive at the tuyeres. We have seen that this diminution of the quantity of C has led to a disappearance of CO_2 —an operation which is attended with an absorption of heat. In consequence of this, the materials leave the zone of reduction less impregnated with heat than they would have been had this cooling by the decomposition of CO_2 not taken place, and by so much are they less fit for fusion in the hearth. But this is only part of the difficulty, for it is obvious that CO_2 is only decomposed by carrying off in the form of CO as much C as that contained in the acid which suffers decomposition. Hence, for each cwt. of carbon as CO_2, which is reduced to CO, the fuel is called upon to furnish a second cwt. to effect the change in question. As soon, therefore, as the charges arrive at the tuyeres, from which this cwt. of carbon has been abstracted in the zone of reduction, the heat is no longer equal to the required duty. It is almost superfluous to say that this deficiency cannot be met by an addition to that contained in the blast, because such addition would not remedy the want of reducing power of the gases in the upper region of the furnace, the bad effects of which have just been described.

The somewhat arbitrary lines in the Fig. 3 are intended to show diagrammatically the effect of the change.

The line *D E*—heat of CO to CO_2—is shortened.

The line *C D* and *E F*, made up of blast heat, and of C to CO in the hearth, have the same length as in Fig. 1, but they are differently constituted, more heat units being furnished by the blast and less by the coke in Fig. 3 than in Fig. 1. The length of these lines, however, is shortened in reality by as much as there has been C dissolved in the upper region, and thus prevented reaching where the fuel is burnt at the tuyeres. I have supposed the lines *C D* and *E F*, being thus reduced to *C' D* and *E F'*, so that instead of the temperature in the hearth being represented in the zone of fusion by *A B*, as in Fig. 1, it is reduced to *A' B'* in Fig. 3.

This temperature would be insufficient, and the only remedy is to restore the coke to its original quantity expressed now by the length of the lines *C D* and *E F*. The heat, however, represented by this extension of these lines would only in part reach the hearth, the remainder being absorbed in re-establishing the equilibrium in the zone of reduction, *i.e.*, it would supply the carbon required, in consequence of the increased quantity of heat brought up by the blast to form CO by the action $CO_2 + C = 2\ CO$. The coke is now raised again to what it was in Fig. 1, and the temperature of the hearth is again extended to *A B*, the direction of the dotted line indicating that the additional coke is partly absorbed in the upper region and partly in the lower. The temperature of the gases suffers little or no change, the real alteration being that the extra heat of the blast (*D' D* and *E E'*) instead of diminishing the coke heat (*C D'* and *E' F*) has shortened *D E*, being the heat of burning CO to CO^2, which costs nothing.

Of course, all the danger just mentioned is entirely dependent upon the furnace in question, one of 80 feet, passing off its gases as completely saturated with oxygen as the nature of the operation admits. Experiment and practice, in my opinion, enable me to state that the gases from such furnaces are almost completely so saturated. In Sections VII. and VIII. the effect of various mixtures of CO and CO_2 on oxide of iron and on metallic iron, are fully described, and they confirm this opinion. The exposure also of calcined Cleveland ironstone in the escape pipes of furnaces of 80 feet, proved that their gases were all but powerless to reduce

the $Fe_2 O_3$ it contained, and the experience of heights increased up to 95 and 103 feet, fails to hold out any hope that more can be done by a longer sojourn of the ore, in such furnaces, than in those of 80 feet. Indeed, if we regard not the observation of a few hours, but of many years, we have the same results in point of oxygen saturation, from 80 feet furnaces, of 12,000 to 25,500 cubic feet, at the Clarence Works, in which latter the ore is exposed half as long again (*v.* Section XXXIII.), as it is in the former, without any advantage, in charging the escaping gases with oxygen, having accrued.

For the correctness of the assumptions applied to the imaginary diagrams Figs. 2 and 3, we have only to appeal to Fig. 4, which is intended to represent the action of one of the 48 feet furnaces, at Clarence, in the same way as Fig. 1 was intended to convey an idea of that of an 80 feet furnace.

The temperature in the hearth of the 48 feet furnace, represented as before by the length of the line *A B* (Fig. 4), is the same as that in the case of the 80 feet furnace (Fig. 1). The form of the strong black curved lines which serve as before to indicate the temperature at different levels in the former case is, however, very different from that in the latter. Instead of the heat being between black and dull red, when the last traces of oxygen from the ore disappear, it is between dull red and full red. The effect of this is that the gases, arriving in the zone of reduction in a highly-heated state, resolve a considerable quantity of the CO_2, generated in this region to CO, and the cooling effect of this action is represented by the diminished length of the line *D E* in Fig. 4, as compared with that of *D E* in Fig. 1.

The heated gases enter the reducing zone in the 48 feet furnace at a high temperature, but, as has been observed, this is greatly lowered by the decomposition of the CO_2 which there ensues; but this is not sufficient to cool them to the point at which they issue from the 80 feet furnace, and the distance of the curved lines at the throat is intended to convey an idea of the difference between the two in this respect.

In the smaller furnace, there are two distinct sources of loss which do not obtain to the same extent in the larger: there is CO_2 reduced to CO, and there is more heat carried off in the escaping gases.

To compensate for this, it will be perceived that the lines *C D* and *E F*, which constitute the heat generated by hot air in the coke, are greatly extended. Both sources, *i.e.*, the blast and the coke, afford more heat than in Fig. 1, but the former is a mere consequence of the latter. The air has the same temperature in both cases, but inasmuch as more coke has to be burnt in the smaller furnace more blast is required, and the greater volume of air of course brings in an increased quantity of heat.

If the total length of the line *C F* (total heat evolved) in Fig. 4 suffered no greater diminution from the sources just mentioned (reduction of CO_2 and sensible heat in gases) than *C F* in Fig. 1, the quantity of heat arriving in the hearth would be that represented by the line *A' B'*; but this is not the fact, and there is just as much loss in the upper portion of the furnace, from the reasons just given, as is indicated by the length of the lines *A' A* and *B B'*, and hence the effective heat evolved in the hearth is the same as it was before, viz., *A B*.

The only other circumstance to which I would direct attention is the entire disappearance of CO_2, in the case of the smaller furnace, at a depth of 18 feet from the top, whereas there are still in the larger, traces at a distances of 40 feet from the top. Of course, the difference of temperature must be looked for as the reason of this.

Believing that the substitution of deposited carbon for that constituting the fuel by the dissociation of CO to have a certain importance in the smelting of iron, it becomes interesting to enquire whether an increase in the dimensions of the furnace is calculated to increase the quantity of C precipitated from its oxide or not.

Reference to Exps. 287 *et seq.* shows when the temperature approaches one of full redness, carbon deposition becomes very faint, and as this heat is arrived at within 10 feet of the same distance from the top of a 48 feet and an 80 feet furnace, viz., 15 feet in the former and 25 feet in the latter, it follows that a large proportion of the additional capacity of the larger furnace will be inert, so far as splitting up CO is concerned.

In Section XXXII. it was stated that in a furnace of 26,000 cubic feet, 7·8 cubic mêtres of gases flowed up per 1,000 cubic feet per minute, whereas in one of 6,000 cubic feet, 23 cubic mêtres passed through the same space in a similar period of time. Under

these conditions, the gases in the larger furnace are three times longer in contact with the ore where carbon deposition takes place, than in the smaller, and hence, it is highly probable that during this time the larger quantity of CO will suffer decomposition in the furnace of greatest capacity. Further, it will be remembered that it has been mentioned in this work, that in the larger descriptions of furnace, the gases were not permitted to escape until their powers of reduction were exhausted, and, in like manner, it will be seen on reference to Exps. 306 *et seq.*, that when calcined Cleveland stone was exposed to the gases as they left the furnace of 6,000 feet, a notable quantity of deposited carbon was absorbed, whereas a trace only was found in the same ironstone when exposed for the same time in a furnace of the larger dimensions, proving that the gases in the latter were no longer capable of being split up into C and CO_2.

For the reasons just given, it seems fair to conclude that there may be a considerably greater quantity of CO dissociated in the larger furnace, but inasmuch as after certain dimensions are reached (about 12,000 cubic feet), the region most favourable for this action remains stationary in point of extent, it is improbable that any addition of capacity, beyond these dimensions, will greatly add to the quantity of C precipitated.

There is another description of chemical action which may possibly be somewhat modified by an addition to the dimensions of the furnace, viz., the extent to which the alkaline cyanides may accumulate. Unfortunately, I possess no analyses showing to what extent capacity acted in accumulating K_2O and Na_2O.

I am not disposed, however, to attach any importance to any deficiency of Cy in the smaller furnaces, for reasons already given, to which may be added the fact that in the case of one experimented upon, which had been blown for only four days* (*Vide* Exps. 605 to 608), the quantity of cyanogen was very small, and yet, as good iron was made, and with as little coke, as when the cyanides were much more plentiful, as happens in furnaces which have been in operation for some time, and in which the cumulative action, already explained, has given rise to the presence of a large quantity of Na and Ka.

* In Section XXXIV. this furnace is stated to have been blown in a few weeks, instead of a few days.

SECTION XXXVIII.—ON THE PROPER CONDITION OF THE MATERIALS TO BE OPERATED UPON IN THE BLAST FURNACE.

Our mineral fuel, as it is found in its natural state, contains more or less volatile matter, almost entirely of an inflammable nature. About 25 per cent. of our clay ironstones consists of O, CO_2, and H_2O, and our limestone loses above 32 per cent., chiefly CO_2, of its weight on being heated. The whole of these, amounting in the Cleveland district to above two tons of volatile matter for every ton of iron made, would be driven off long before the materials reached the tuyeres, if they were used in their raw state—a mode of procedure which would be attended, of course, with a strong refrigeratory action.

To avoid this, and other inconveniences, our coal is coked, our ironstone, and often the limestone, are calcined, and in this Section I propose considering what is gained by these modes of preliminary treatment, and how they ought to be performed.

THE FUEL.—About the year 1620, owing to the increasing price of charcoal, Dud Dudley proposed the use of mineral coal in smelting iron. Had this discoverer met with encouragement, instead of persecution, from those interested in the question, it is difficult to imagine that he would not ultimately have been led to treat mineral fuel as they had previously done the vegetable, viz., char it. Instead of this, Dudley never, it would appear, obtained more than seven tons a week from his blast furnace, fed with pit coal in its raw state, and the process was abandoned in 1657, and thus this great discovery, which has since added so immensely to our national position, remained dormant for nearly 80 years, when Abraham Darby, about 1735, crowned the work of his unfortunate predecessor, by coking the coal before using it.

It is impossible to overrate the importance of Darby's work at the period of its accomplishment, but since his day, events have transpired which have somewhat altered its value. The coal employed by Darby was that of the Midland Counties, resembling,

so far as amount of volatile matter is concerned, the fuel used in the ironworks in the neighbourhood of Glasgow, and which, anterior to 1829, was also exclusively employed in the form of coke.

Nielson's discovery of the hot blast enabled the iron manufacturers in Scotland, at the time, to dispense with the preliminary process of coking, and moreover reduced the consumption of furnace fuel from 3 tons of coke per ton of iron to 2 tons of raw coal, thus rendering available, as it might be thought, the combustible gases of the coal, instead of imposing on the fixed carbon the extra work of expelling so much volatile matter. Thus the actual heat in the blast was receiving less credit than it was entitled to in the Scotch furnaces; but, on the other hand, the advocates of hot air claimed more than was its due, in supposing that the Welsh coal, containing only about half the quantity of volatile matter existing in that of the North, could not be employed with the cold blast.

From what has preceded on the heat requirements of the blast furnace, it would be easy, if we knew the quantity of heat evolved by the combustion of coal, to calculate how many heat units are absorbed in volatilizing its gases. All we would have to do would be to calculate the total heat evolved by the combustion of so much carbon and so much hydrocarbons as are contained in the coal under examination, and from it deduct the number of heat units afforded by the combustion of the coal itself.

According to Watts,* the calorific power of raw coal has not been satisfactorily determined yet, but, according to the latest experiment, he puts it down at 5,724 calories. This seems to me to be too low, and I have arrived at this conclusion from the experience obtained in the manufacture of gas for illuminating purposes.

By the favour of the authorities at the Newcastle Gas Works, I find 15 parts of coke are burnt under their retorts to expel the gas from 100 parts of coal. For the purposes of this somewhat rough kind of calculation, let it be assumed the coal used in this establishment to consist of

Ash	3
Solid carbon	57
Hydrogen and hydrocarbons ...	40
	—100

* Article, Coal: Dictionary of Chemistry.

If the above-named combustible constituents were burnt, we should have—8,000 calories for each unit of carbon, and something like 11,000 for the hydrocarbons, &c.

57 × 8,000	... = ...	456,000	
40 × 11,000*	... = ...	440,000	
			896,000

From this must be deducted the heat evolved by the combustion of 15 of coke, but of this there is a considerable waste by radiation and by the chimney—say one-third.

15 of coke = C 14·2 × 8,000 units	113,600	
Less one-third wasted	37,800	
		75,800
Net calories evolved by burning 100 of coal		820,200

This mode of calculation brings out the calorific power of such a coal as that considered to 8,202, instead of 5,724, so that, in round numbers, one pound of coal or one pound of coke is nearly the same in heating power. This agrees pretty closely with the experience of locomotive engineers, who, in the North of England, generally speaking, regard raw coal as doing rather more work than the same weight of coke.†

Admitting the general correctness of the above estimate, each unit of volatile matter requires 1,895 heat units (75,800÷40) for its expulsion. If then 22·5 cwts. of coke were used to smelt one ton of iron from Cleveland stone, as happens in a furnace of 80

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* The constitution of coal gas by weight has been considered as follows, and the heat of combustion is that set opposite to each:–

Hydrogen	5 × 34,000 =	170,000
Marsh gas	61 × 13,000 =	793,000
Olefiant gas	10 × 12,000 =	120,000
Carbonic oxide	12 × 2,400 =	28,800
CO_2, N, &c.	12 × nil. =	nil.
100		1,111,800÷100–11,118

Taken at 11,000.

† Since writing the above, I have examined the experiments of M.M. A. Scheurer Kestner and Charles Meunier, published in the Annales de Chemie et de Physique for December, 1870, on the heat of combustion of coal. In one case, where the ash was 5·72 per cent., and the volatile matter 22·26, the heat units per unit of coal are given as 8,587, which is something like the number obtained by the rough form of calculation I have used.

feet, and the coal producing such coke contained 30 per cent. of hydrocarbons, as usually happens with our coking coal, 32 cwts. to 33 cwts. of raw coal would represent this weight of coke. From this quantity of raw coal 10 cwts. or thereabouts of gaseous matter would need expulsion, requiring for its performance ($10 \times 1{,}895$) 18,950 units. The use of raw coal undoubtedly reduces the temperature of the escaping gases; but, on the other hand, they are increased in quantity, so that little heat would be available from this source. In consequence, the necessary heat required to volatilize the gases of the raw coal would have to be provided by burning so much more carbon at the tuyeres. As no CO_2 would be generated by the combustion of this extra quantity of C, we should only have the C to CO, which, with the heat of the blast, would afford about 3,000 calories per unit of coke.

Now, 18,950, the number of calories needed to expel the gas from the raw coal, divided by 3,000, gives 6·32 cwts. of such coke as being required for the purpose in question, or if employed as raw coal, the heat of 9 cwts. of such raw coal would be absorbed in getting rid of the hydrocarbons, &c. This 9 cwt. of coal will also require heat for evaporating its hydrocarbons, so that a blast furnace using 22·5 cwts. of coke per ton of iron ought, were its fuel used uncoked, to consume about 44 to 45 cwts. to do the work.

This view of the heat absorption appears to be confirmed by what was done in the smaller furnaces in Cleveland and Scotland. In the former, 29 cwt. of coke was the ordinary consumption for No. 3 iron, which, with an ironstone yielding 50 per cent. of metal, instead of 41 per cent., like that of Cleveland, would have been reduced to about 26 or 27 cwt. per ton of iron. In Scotland, with their richer stone, they required 53 cwt. of raw coal, containing 65 per cent. of coke, so that the 53 cwts. would afford 34·45 cwt. of coke, or say 8 cwts. above that which would be burnt in Cleveland for an ore of 50 per cent. From this I infer that the 8 cwts. must have been required to vaporize the hydrocarbons, &c., contained in the 53 cwts. of raw coal. This mode of computation supposes that the escaping gases from the Scotch furnaces contained the same quantity of heat as those of similar dimensions in Cleveland, of which I had no means of judging, as the Scotch furnaces are worked open-topped.

It would, consequently, seem clear that the consumption of coal,

required in the furnace itself, is actually considerably higher when it is used raw than when coked, for 27 cwt. of coke, obtained from coal containing 65 per cent. of fixed carbon, is only equal to 41·5 cwt. of coal—against 53 cwt. of the latter, actually needful for the process.

On investigating the subject a little, this is not difficult to understand. In the coke ovens, the hydrocarbons are consumed, and emit far more heat than is absorbed; for the combustion of the gaseous matter, being perfect, gives out 11,000 units, whereas, the coking in the blast furnace is chiefly effected by burning C to CO at the tuyeres, from which only about 3,000 units are received.

The subject of the actual yield of coke in the manufacture of this article will be considered presently; in the meantime, it has been assumed that all the fixed carbon in the coal has been received from the ovens as coke, which is rarely done.

In the preliminary operation of coking there is an enormous waste of heat, unless it is applied to some useful purpose, which, in this country, at least, is seldom cared for. Omitting waste from radiation, &c., the following shows the heat development from the 22·5 cwts. of coke and 44 cwts. of raw coal, which, for blast furnace work, were considered equivalent quantities; and supposing the evolved gases, from both coke and coal, capable of subsequent utilisation, and, therefore, combustion into CO_2 in the one case, and CO_2, with H_2O in the other, we have—

	Heat units. Cwts.
22·5 coke, containing 20·9 cwts. of C × 8,000 units ...	167,200
Obtained from 34 cwts. of coal coked: hence, 1 of coal = (167,200 ÷ 34)	4,917
44 cwts. raw coal, containing 26·6 cwts. of C × 8,000 units	212,800
„ „ 15·4 hydrocarbons × 11,000 „	169,400
	382,200
Less 15·4 cwts. hydrocarbons, absorbing for their expulsion, 1,895 units × 15·4 cwts. = ...	29,183
	353,017
Obtained from 44 cwts. raw coal, hence 1 of coal = (353,017 ÷ 44)	8,023

Thus, between burning raw coal and coke in a blast furnace, and using the escaping gases, but wasting the surplus of heat at the coke ovens, the actual loss is that represented by (8,023 – 4,912) 3,111 units, or about 39 per cent. of the whole.

Recently, Mr. Wm. Ferrie, of the Monkland Iron Works, has erected a furnace formed by building four chambers or retorts on the top of one of the old furnaces, about 20 feet in depth, and each having a capacity of 500 cubic feet, the body of the furnace itself containing 7,000 cubic feet, making in all, 9,000 cubic feet.* These retorts are heated by a portion of the escaping gases being burnt in external flues, and the result is a saving of about 19 cwt. of coal to the ton of iron. This was demonstrated under circumstances so convincing that we may accept it as a fact beyond all dispute, that while 52·5 cwts. of raw coal were required to make a ton of iron, in a furnace of 53 feet in height, 33·5 cwts. sufficed in what Mr. Ferrie calls his self-coking furnace, with a height of 83 feet.

The fuel used contained 65 per cent. of coke, so that we may regard 21·8 cwts. per ton of iron as the equivalent quantity of coke to 33·5 of coal. After allowing for the lesser weight of slag, 15 cwts. per ton of iron, instead of 30 cwts., this makes their consumption of coke pretty nearly the same as that of the Cleveland district, in a furnace of similar height.

From this I inferred† that the chief virtue of this invention consisted in its height, but a more careful consideration of the circumstances attending the use of raw coal, induces me to regard this view as erroneous, because I have shown above, that for every unit of volatile matters expelled, 1,895 calories are absorbed, hence, in this particular case, we have 11·7 cwts. (the gas in 33·5 cwts. of coal) × 1,895 gives 22,171 units, required for this purpose alone.

The temperature of the gases leaving Mr. Ferrie's furnace over a space of seven hours I determined to be 310°C. (590°F). Their weight per ton of iron would be about 147 cwts., and the sp. heat, containing as they do a considerable amount of hydrocarbon, would be about ·26, which gives (147 cwts. × ·26 S.H. × 310°) 11,848 units per ton of metal. This is something more than

* This furnace was fully described by Mr. Ferrie; *vide* Journal of Iron and Steel Institute, May, 1871.

† *Vide* Discussion on Mr. Ferrie's paper, May, 1871.—Journal of Iron and Steel Institute.

would be carried off in the escaping gases from one of the 80 feet Clarence furnaces for a similar quantity of iron. The temperature of the blast at Monkland, I may observe, was 480°C. (896F.) at the time of my observations.

Leaving out of view any excess of heat on the gases, as an unavoidable waste attendant on the peculiar form of the apparatus, we have a distinct advantage of the 22,171 units of heat required for vaporizing the volatile constituents of the coal, which must have been obtained from the combustion in the flues surrounding the retorts, seeing that a ton of iron has been made with as small an expenditure of fixed carbon as if coke had been used.

Taking each unit of the gases capable of giving, by its combustion, 11,000 heat units, we would have (11·7 × 11,000) 128,700 heat units, of which 22,171 are absorbed in the work of the retorts, or about 17 per cent. of the whole. As there would be some waste at the chimney, probably about 25 per cent. of the total volume of the hydrocarbons would be required for the coking process, leaving the remainder and all the CO escaping from the furnace applicable for other purposes.

In effect, then, this modification of the blast furnace, by Mr. Ferrie, may be regarded as having, by its height alone, done exactly what has been accomplished in Cleveland, and by the retort arrangement it has obtained the necessary heat for coking the coal.

Irrespective of the heat evolved by the generation of CO_2 in the upper part of the furnace, by reduction of $F_2\ O_3$, that obtained by the generation of CO would be as follows :—

	Cwts.	
In 53 feet ordinary furnaces, 52·5 cwt. of coal = coke	34·12	
C in CO_2 of flux, and C in CO_2 from deoxidation, reduced to CO, carrying off by $CO_2 + C = 2\,CO - C$	2·22	
Leaving for oxidation at tuyeres	31·90	
31·9 cwts. coke × 3,000 units (the heat obtained by burning it with hot blast)		95,700 units
In the 83 feet furnace of Mr. Ferrie, 33·5 of coal = coke	21·80	
C in CO_2 of flux, carrying of C	1·20	
No CO_2 from deoxidation of $Fe_2\ O_3$ reduced to CO.		
Leaving for oxidation at tuyeres	20·60	
20·6 cwts. × 3,000 units.		61,800 units

Thus it would appear that in the hearth of one furnace it requires 95,700 units to effect the same work which is done in the other by 61,800 units. To these 61,800, however, must be added the 22,171 units, shown to have been evolved and utilized by the distilling apparatus, which brings up the whole to 83,971.

In the 53 feet furnace, with an open tunnel head, a good deal of the gases would be expelled by the high temperature which prevails there. The gases in 52·5 cwt. of raw coal would absorb above 30,000 heat units for their evaporation, and supposing one-third of these were obtained from the ignited gases, we have the 95,700 units brought up to 105,700.

Exclusive of the expulsion of the gases, the saving by Mr. Ferrie's furnace will be from mere addition of height :—

$$105{,}700 - 83{,}971 = 21{,}729 \text{ units,}$$

and from the combustion of the gases the saving was estimated at 22,171 units, so that there seems fair reason for believing that about half the saving of fuel may be set down to increased capacity, and half to the heat derived from the combustion in the flues surrounding the retorts.

The presence of this large volume of hydrogen in the escaping gases, when using raw coal, is then not only no source of heat, but its distillation exerts, as we have seen, a very considerable cooling influence, met in the ordinary blast furnace, by an additional expenditure of about half a ton of coal, equal to one-fifth of the total consumption.

I am, however, by no means persuaded that this hydrogen, either in its pure form or as CH_2 or CH_4, has to be regarded as useless. If we refer to Section XXVIII., it will be observed that the total heat development in the hearth in an 80 feet furnace, using 22·32 cwts. of coke, was accounted for when contrasted with the heat appropriation by within 3,743 cwt. heat units, an amount set down as arising from certain items which had been overlooked.

Admitting, however, that no omission had been made, and that these 3,743 units were either absorbed by a reduction of CO_2 to CO, or made their appearance in the escaping gases, as the case might arise, it is obvious the margin is a very insignificant one, being not quite that represented by 1¼ cwt. of coke burnt at the tuyeres.

As nearly as may be, this margin, according to the statement, arises equally under the two heads of reduction of Fe_2O_3, includ-

ing carbon impregnation, and fusion—along with all other sources of absorption.*

Now, in the event of anything taking place to disturb the equilibrium of the upper portion of the furnace, such as a quantity of ore arriving at the zones of higher temperature unreduced, CO_2 disappears to some extent at once.

It has been repeatedly set forth in these pages that a limit to the economy of fuel lay when the CO had taken up its full quantity of O, and that in the case of smelting Cleveland stone, this point was arrived at when 100 vols. of the two oxides of carbon contained from 28 to 32 of CO_2 (100 CO=40 to 45 CO_2). This saturating of the gases with O takes place, it is conceived, in the upper 12 or 13 feet of the height of the building. Supposing, now, such an accident as that just alluded to, to have taken place, and attended with a reduction of the quantity of CO_2 to CO, and let it be imagined that this has been going on to the extent of ·5 cwt. of carbon—not a large quantity per ton of iron—and that it continues in activity for a time.

The effect of this change (CO_2+C=2 CO) is that ·5 cwt. less carbon reaches the hearth than would, under a more perfect state of working, be oxidized there, which, with the heat in the blast, means a suppression of 1,500 units per ton of iron. In addition to this, we have the refrigeration caused by so much CO_2 being reduced to CO, which amounts to (3,200÷·5 cwt.) 1,600 units for the half cwt. of C. Thus, there is a positive loss felt all over the furnace of (1,500+1,600) 3,100 units—quite enough of itself to affect, not, perhaps, the actual process of smelting, but certainly enough to lower sensibly the quality of the iron.

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* The amount may be stated as follows:—

Conversion of C into CO ... cwt. heat units		45,024	
Contained in blast		11,919	
		56,943	
Less carried off in gases		8,860	
		48,083	
Required for fusion and other items, except reduction and carbon impregnation		46,304	
Margin			1,779
Heat evolved by C in CO converted to CO_2		36,512	
Do. required for reduction of Fe_2O_3 and carbon deposition		34,548	
Margin			1,964
Total			3,743

Now, all this time the gases, so far as the relation of CO and CO_2 are concerned, are more highly reducing than they were before, inasmuch as there is ·5 cwt. less C as CO_2 than previous to the supposed cause of derangement. This is true, but their activity is sensibly impaired in consequence of the loss of heat, so that, even with the additional CO they contain, they are no longer equal to the work.

Matters, however, are different in a furnace usuing raw coal, as will appear from the analysis of gas taken from one of the Coltness furnaces.

Exp. 704.	CO_2	13·6	
	CO	28·9	
	H	10·3	
	N	47·2	
		——100 volumes	

This, perhaps, scarcely represents the average composition, for the CO to CO_2 is as 100 to 47, which is probably above what it ought to be; but what I wish to point out is, that beyond the CO found in a large Cleveland furnace (produced by the combustion of C in such quantity as is competent to melt the iron the CO can reduce) there is in the gases at Coltness a large amount of deoxidizing gas (10·3 vols. H.), which brings the oxidizing element CO_2 down to 34·7 vols. per 100 vols. of those of the reducing order, viz., the CO and H. In such a case of derangement as that supposed, the large quantity of H always present is in excess of the actual quantity required to keep in check the oxidizing tendency of the CO_2, even under the circumstances described, and the result is a regularity of working, so far as the production of No. 1 is concerned, quite unknown in Cleveland where coke alone is used.

This, at least, I would suggest as the probable cause of Scotch works, using raw coal, making occasionally for weeks together nothing but No. 1 iron, an event which I believe would be sought for in vain in the books recording the performance of furnaces on the banks of the Tees.

Exp. 705. In order to ascertain whether the carbon or the hydrogen in coal gas exercised the stronger reducing action, one litre of this substance, well dried, was passed over a quantity of

calcined Cleveland ore previously heated to expel H_2O, all air being driven out by a continuous current of gas. The temperature was under that of redness; indeed, a fragment of zinc placed on the top of the tube did not melt.

The ore lost 1·2 grains, and the H_2O collected weighed 1·3 grains=1·15 O. The gas contained 4 per cent. of its vol. of CO_2 before the operation, and 4·1 after, so that the reducing action was almost exclusively due to the H.

Of the reducing power of H itself, and of its power in assisting CO in removing O from Fe_2O_3, instances were given in Section XXII., all of which point to the conclusion that its presence may be beneficial, by mantaining a reducing action in the gases, when accidental circumstances might weaken their activity in this respect.

In the estimates of comparative heat development, which are given in this section, it has been assumed that all the fixed carbon found in coal is obtained as coke. This, however, is not the fact in the ordinary way of manufacturing this substance. As is well known, the coal is introduced into a vaulted chamber immediately after a charge of coke is drawn, and the door, through which the coke is removed, carefully closed by clay luting above the level occupied by the coal. The heated brickwork induces distillation, and the liberated gas takes fire, and burning on the surface of the fresh charge, affords the necessary temperature to expel the whole of the volatile matter. When suitable coal is used, there is obtained that bright, hard, silvery-looking coke so well known, and so highly prized by furnace managers. The operation is continued for the space of from 72 to 96 hours, and although a certain amount of care is taken to prevent the influx of air acting on the coke, in practice, there is a notable waste of the latter, amounting to from 5 to 7½ per cent. Thus, a furnace in the Cleveland district, consuming, apparently, 22·5 cwts. of coke per ton of iron, has in reality incurred a waste of coke at the ovens of above 1½ cwt. of this material, or about 2¼ cwts. of coal. The actual cost, therefore, on each ton of iron, incurred in coking coal, besides the waste of heating power, already mentioned, will not be short of 2s. for expenses and waste of fuel at the ovens.

Attempts have been made to avoid this loss of coke in the process of its manufacture, and to these I would now briefly allude.

The first and simplest of these improvements consists in conducting the products of combustion in the ordinary oven through flues round the sides, and under the sole. This greatly expedites the process, and, no doubt, by shortening the period of the coke's exposure to the action of the air, considerably lessens the waste.

There are other modes of manufacturing coke practised in France and Belgium, in which all access of air is prevented. Two of these I have recently described in a paper, read before the Institution of Mechanical Engineers,* in which, almost the whole of the fixed carbon is obtained as coke, the exception being a very minute loss incurred in drawing.

My firm has tried these plans, but found the useful effect in the furnaces inferior to that obtained from the coke made in the ordinary oven. In consequence of this, all the more recently erected ovens have been constructed upon the old fashion; and I have endeavoured to ascertain what are the circumstances which reduce the value of the commodity made according to the more modern improvements below that made in the more simple oven.

Frequent mention has been made in these pages of that action of CO_2 on C, by which an equivalent of the latter is dissolved, and the former reduced to the condition of CO ($CO_2 + C = 2\,CO$). When the temperature is sufficiently elevated, this solution of C by CO_2 goes on very rapidly, but decreases as the heat falls to that prevailing in the upper portion of the furnace, in which CO_2 is generated by the deoxidation of the ores of iron. I have proved, however, that the carbon, as it exists in different qualities of coke, is not influenced in the same degree by this solvent power of CO_2; that of the soft description known as black ends being more easily attacked than the hard silvery-looking kind formerly mentioned.

Exp. 706. 2¼ grammes of hard coke, previously exposed for two hours in a covered crucible to a high temperature, was placed in a combustion tube. All air being expelled from the apparatus, a stream of thoroughly dried CO_2 was passed over the coke for 15 minutes at a red heat, and for 35 minutes at bright red (maximum of a Hofman's double furnace). Two litres of CO_2 were passed over the coke, and from this only 26 ccs. of CO were collected, the remainder of the CO_2 being unchanged.

* *Vide* their Transactions, 1871.

In Exp. 244, a quantity of calcined Cleveland stone, impregnated with carbon, and containing the same quantity of C as that present in the coke of Exp. 706, was treated exactly in the same way as that described in the previous trial. It gave 83 ccs. of CO.

Exp. 707. Deposited carbon in calcined Cleveland ore, freed from Fe, &c., by boiling H Cl, and therefore consisting of C and Si O_2, was exposed for 11 hours to a current of CO_2, at a temperature of 500°F. No decomposition of the CO_2 took place.

Exp. 708. Hard coke, pulverized to size of mustard seed, exposed at a temperature of melting zinc for three-quarters of an hour to a current of CO_2, gave a mere trace of CO.

Exp. 709. Soft coke, similarly treated as previous Exp. (708), in 1¼ hour, gave 92 ccs. of CO, determined by explosion with O, and absorption by K H O.

An experiment was made (No. 448) at the Wear furnace, which seemed to indicate that at a temperature of 500°C. (932°F.), CO_2 was, to a slight extent, reduced to CO, which, I consider, was due to the presence of soft coke.

I am unable, by actual analyses of the furnace gases, to give any very striking instance of the effect of expressly using soft coke on the quantity of CO_2. Upon one occasion, however, soon after lighting several new ovens at one of the collieries of my firm, and thereby producing more than the usual quantity of indifferently burnt coke, all the 8 furnaces at the Clarence Works worked disadvantageously in point of consumption of fuel.

The gases were sampled and analysed. As a specimen, the following shows the result of ten experiments made on these of No. 7 furnace, having a capacity of 15,500 cubic feet.

Exp. 710.	CO_2	CO	H	N
	9·6	30·6	1·5	58·3
	9·5	30·5	1·5	58·5
	10·5	27·6	1·5	60·4
	10·6	28·4	·9	60·1
	11·0	30·8	·8	57·4
	11·2	30·6	1·0	57·2
	10·0	29·3	1·5	59·2
	10·0	31·3	1·4	57·3
	10·8	27·0	1·4	60·8
	10·8	27·4	1·6	60·2
Average...	10·4	29·35	1·31	58·94

In these analyses, the proportion of CO_2 to CO is as 35·4 to 100, instead of 40 to each 100 of CO.

In the attempt which has just been made to discuss the relative economy of using mineral fuel in its raw state or in the form of coke, the question has been examined as one of heat evolution alone. This is very useful in order to determine the exact loss of heat incurred by calling in the aid of the coke oven; but it by no means follows that the waste which ensues can be avoided, for the use of the coal in its uncoked form is not always practicable. In Scotland—in Wales—in short, wherever coking is dispensed with, the coal is what is known as one of a dry-burning nature, *i.e.*, the state of semi-fusion in which the Durham coal enters before it cokes is entirely, or almost entirely, absent. The consequence is that the fragments of coal thrown into the furnace show little disposition to unite with each other. The reverse is the case with the produce of the collieries in the county of Durham, which is so bituminous that a barrow of it thrown into a furnace would probably form one agglomerated mass, and this is not only followed by an irregular mixture of the materials, but causes the whole of the contents to form a species of arch or "scaffold," as it is termed, interfering with their descent towards the hearth, a mode of working which is always accompanied by considerable derangement of the process.

The coal, too, in the North of England is of a much more friable nature than that of many other iron-making districts, and in consequence of this peculiarity it is received at the works in such small pieces as would greatly impede the passage of the blast.

Such questions as that now being considered cannot, however, be confined within the limits of a mere examination as to whether a waste of heat is incurred by any particular form of treatment. It and all other similar enquiries, after passing through the ordeal of philosophical research, must be made to pass through the test of commercial practicability. It is obvious, if the carriage from the mine to the smelting works forms an item of considerable expense, it will be for the ironmaster to determine whether it will pay him best to convey his fuel in its condensed form of coke or as raw coal, for unless the combustible gases, given off by the latter in the blast furnace, can be rendered available, it is quite possible that it may be more economical to submit to the waste connected with the use of the coke oven. This latter mode of procedure may possibly, in

a short time, have the further recommendation of a considerable portion of the heat now passing off unutilized from the coking process, being applied to raising steam for the engines engaged in drawing coal and water at the colliery itself.

Upon more than one occasion proposals have been made to economize fuel in the blast furnace by the injection of heated or combustible matter at the tuyeres.

Many years ago, while visiting the Dombrova Works, in Poland, I found the manager of that concern engaged in applying a process largely used, it was stated, at Decazeville, in France; the invention, if I remember rightly, of Mons. Cabrol of that place. It consisted in passing a portion of the blast through a coal fire, burning in a furnace, contained in a large iron chamber strong enough to support the pressure it had to encounter from the compressed air from the blowing cylinders flowing through it.

I have never been able to understand how the inventor of this mode of applying heat to the smelting of iron expected to accomplish his object by the means he employed. The character of the gases he would obtain would, of course, depend upon the relative quantity of atmospheric air he made to traverse the coal fire. They might consist of CO and the hydrocarbons of the coal, or of CO_2 and H_2O; or what is still more likely, there would enter the furnace at the tuyeres a mixture of all. Admitting that the whole of the heat evolved by burning C to CO_2, and H to H_2O in the external chamber, found its way into the blast furnace, there would ensue the refrigeration due to H_2O being reduced again to the condition of H, and of CO_2 to that of CO, in which forms they would leave the throat. If, on the other hand, hydrogen or its compounds with carbon, or carbonic oxide, were injected, any water formed by the action of the blast would pass again to the state of H immediately it met with C or Fe; and similarly CO_2, derived from the oxidation of CO, would lose half its oxygen from the same cause.

Upon more than one occasion the idea has been suggested of collecting the gases evolved from coking coal, and driving them into the furnace. The same objection as regards the use of H, which has just been mentioned in connection with Mons. Cabrol's proposal, is applicable to this scheme; and any benefit to be obtained from the quantity of C contained in the coal gas would certainly be more than swallowed up by that required to expel the

gas from the coal, by the probable deterioration of the quality of the coke, and by the costly apparatus in the form of gasholders and pumps required to force it into the furnace.

At Couillet, in Belgium, some years ago, a piece of mechanism was attached to the blast pipes, by means of which small coal was carried into the hearth, along with the blast; and, more recently, it has been suggested to apply Mr. Crampton's idea of obtaining heat by burning finely ground coal in a current of atmospheric air, the powdered raw coal being injected at the tuyeres.

Such a mode of procedure as that involved in either of the last two mentioned plans is open to the insuperable objection of the great heat absorption which takes place in the vapourizing of the volatile constituents of coal, and which has been shown to be such, that even with the entire combustion of the hydrocarbons to H_2O and CO_2, it reduces, as we have seen, the calorific power of this form of combustible almost to that of coke. The cooling effect of so much hydrocarbon having to be evaporated in the hearth of the furnace, would be diminished still further if, as is the case, the hydrogen had not to suffer permanent oxidation near the tuyeres.

There is, however, a difficulty connected with the introduction of inflammable matter, at the lower region of the furnace, which is more or less applicable, whether the combustible is in the gaseous or solid form. The particulars of a calculation were given in the present Section, showing to how great an extent the intensity of the heat in the zone of fusion of a blast furnace was promoted by the material coming down to the tuyeres largely charged with intercepted heat, taken up during its progress, towards the hearth. If instead of introducing the fuel at the throat, it is injected at the seat of combustion, this preliminary saturation by the ascending heat will be wanting, and by so much will that developed at the tuyeres be deficient. This latter objection, in my judgment, is a fatal one to the addition of fuel near the hearth.

ORE.—In the greater number of the accounts given of the process for producing iron in its malleable form direct from the ore, and which is still practised exclusively by the natives of Asia and Africa, the preliminary treatment of calcining the ore, before it is introduced into the shallow charcoal hearths, appears to be omitted; at all events, this is so when these simple ironworkers have to deal with rich oxides. It is incredible among people of

even moderate intelligence, that either by accident or design, roasting the ore previous to its reduction would not have been discovered, and put in practice during the many ages in which this primitive mode of obtaining this metal has been in use, had such a mode of treatment been found beneficial. In Borneo, where clay ironstone is the ore used in this direct process, previous calcination is employed, in order to expel the large quantity of volatile matters it contains.

In the Catalan furnaces, as they continued until very recently to be worked in various localities in Europe, the daily quantity of malleable iron greatly exceeded that obtained by less civilized nations, and in this more perfect apparatus, when using even the Elban and other rich ores, calcination had been practised from time immemorial, and, indeed, in the so-called Catalano-Ligurian form the ore was partly deoxidized by the waste heat from the hearth itself, before it entered upon the last stage of the process.

Before even the Catalan had expanded itself into the Osmund Furnace, kilns 6 or 8 feet high were in use for the purpose of relieving the more complicated form of apparatus itself, viz., the furnace, of part of the work, and this was continued up to the time when the Stückofen, the immediate predecessor of the blast furnace, came into use.

In Great Britain, where by far the largest quantity of the yearly produce of pig iron is obtained from an ore containing 25 per cent. of volatile matter, chiefly CO_2 and some H_2O, it is obvious that so simple an operation as calcining would, at all events, when blast furnaces of moderate dimensions were employed, be considered as indispensable, were it for no other reason than to avoid loss of time and waste of fuel in a piece of apparatus of so costly a character as the furnace itself.

But the mere expulsion of inert matter was not all that was aimed at. Many of the ores of iron contained sulphur in greater or less quantity, the evil effects of which were recognised by very early smelters, and in some cases after being roasted, the ores were washed, to carry off any adhering $Fe\,SO_4$, formed during the process of calcination.

I have already shown that this dread of traces of sulphur was, perhaps, sometimes unnecessarily exaggerated, but the entire absence of this ingredient, even in the richest ores, does not

constitute a reason for dispensing with the practice of calcination. At Dannemora and Mariedam, in Sweden, and at Fullonica, in Italy, I purposely inhaled the vapours from the roasting kilns, containing pure magnetic and specular oxides of iron, without being able to detect any SO_2, a very slight trace of which makes itself felt to the smell. In such cases, the sole effect aimed at is to render the ores themselves more open in texture, so as to permit freer access of the reducing gases, and the difference of susceptibility to deoxidation, caused by alteration of molecular structure, would indicate that this time-honoured custom is founded on strictly correct principles.

It has been demonstrated in various sections of this work that the old furnaces of 48 or 50 feet were too small to permit a maximum effect being obtained from the fuel consumed therein, even when using roasted stone. A dozen years ago, this subject had not been so well investigated as it has been more recently, and following the advice and example of a friend, himself an ironmaster, that it was a waste of money to submit the Cleveland stone to calcination before using it in the blast furnace, I proceeded to make a trial with raw ironstone. The result was a diminution in the make, and the saving of the small coal required in the kiln was far more than wasted in value by the higher consumption of coke in the furnace.

Soon after the introduction of the lofty furnaces of more modern days, I made a second attempt with uncalcined stone, in the hope of utilizing the heat known to be carried off in the escaping gases. The experience, in a commercial point of view, was much less unfortunate than when a similar experiment was tried with the smaller furnace, but it was not of that order to induce me to prosecute the experiment.

Within the last year the subject has received much attention in a modified form at the hands of a very painstaking manufacturer, Mr. Jones of the Normanby Iron Works, near Middlesbrough. Mr. Jones, in furnaces of only moderate dimensions—73½ feet high, and containing 10,000 and 12,000 cubic feet—has for some time past used his ironstone raw in such proportion that one-third of the produce of his make is derived from uncalcined stone; but, on the other hand, his limestone is all burnt.

Upon the occasion of my being courteously permitted by Mr.

Jones to make a series of observations upon the temperatures, &c., of his furnaces, I found the blast he was using at the one to be as follows :—

Exp. 711.

Hour.	Back tuyere.	West side	East.	
11 a.m....	939 ...	861 ...	—	Average.
2 p.m. ...	914 ...	867 ...	953	907 F.=486°C.

and at the other :—

Exp. 712.

10·15 a.m....	939 ...	879 ...	—	Average.
4·15 p.m....	914 ...	854 ...	—	896F.= 480°C.

The mere driving off of the CO_2 and H_2O from a clay ironstone is so simple an affair that the operation can be conducted in the rudest fashion. This often consists in forming heaps of the mineral mixed with the necessary fuel, and setting fire to the mass. In Staffordshire, this is the practice generally followed to this day, and in Scotland, where the black band ironstone contains coal enough, and more than enough, for its calcination, large mounds are formed as it is brought out of the pit, and fire applied when enough has been accumulated.

The mode of roasting in mounds or "clamps," just mentioned, requires no building, but it is costly in fuel, in labour, and is, moreover, attended with an inconvenience, not sufficiently appreciated, I imagine, of the ironstone either being over hardly calcined, or, what is worse, actually running into a scoriaceous mass.

The use of a kiln of even moderate dimensions frees the process from much that is objectionable on the three points just named, and they may be said to be reduced almost to a minimum by a kiln, recently erected from the designs of Mr. Borrie, at the Eston works of Messrs. Bolckow, Vaughan, & Co. (Limited). In it the building is raised to an altitude of 40 or 50 feet,* so that the volatile matters, before leaving the materials, part with almost the whole of their sensible heat to the fresh charges thrown into the top of the kiln, by which means nearly all unnecessary waste of fuel is avoided. By the aid of sliding doors, the suggestion of Mr. Borrie, the calcined stone discharges itself into the barrows in which it is conveyed to the furnace.

* Ten years ago a kiln 50 feet high was built at Washington, and ironstone burnt with a minimum of fuel; and since then lofty kilns have been erected at Teesside Clarence Works, and elsewhere.

The labour is thus reduced to less than what it would be if the ironstone were charged direct, by the most economical method, into the throat of the blast furnace, inasmuch as it is diminished in weight by something like one-fourth.

The fuel required is insignificant; for one ton of small coal, worth 3s. or 4s., suffices to calcine 29 tons of stone, representing thus something like 5d. per ton on the iron made, or ·66 cwt. of coal per ton of raw stone.

Under these circumstances, I fail to see how the economy in obtaining one-third of the produce of a furnace from raw stone can be attained with a saving beyond (5d.÷3) 1·67d. per ton on its entire make, unless there are other attendant advantages in the adoption of this system.

Mr. Jones maintains that his consumption of coke is quite as low or indeed lower, than that at many furnaces using calcined ironstone and raw limestone, as, indeed, it ought to be, so far as the presence of combined CO_2 can make it. The Cleveland stone contains about 23 per cent. of CO_2, and about 31 per cent. of Fe; hence in the proportion in which the raw stone is introduced into the Normanby furnaces, about 4·5 cwts. of carbonic acid per ton of iron will be found in some shape in the gases, either as CO or CO_2; but by burning the limestone, say 11 cwts., if thoroughly calcined, 4·8 cwts. of CO_2 are got rid of.

This is not the measure of the difference, because a larger quantity of fuel is required to expel CO_2 from its combination with Ca O than from ironstone.

In order to compare the effect of using raw stone, the following experiment was made on two of the Clarence furnaces—both of 25,500 cubic feet—which had been working with the same burdens and with the same results for some months. From one of these, one-third of calcined stone was withdrawn, and its place taken by an equivalent quantity of raw, the flux in its natural state being used at both. The second week, from making grey, the iron fell to chiefly mottled and white.

	Exp. 713. In furnace using part raw stone.	Exp. 714. In that using all calcined.
No. 4 iron ...	65 tons	356 tons
Mottled ...	162½ „	61 „
White	206 „	—
	433½ „	417 „

The coke consumed was almost exactly the same in each furnace per ton of iron; but, from that using raw stone, the large quantity of white iron produced led to a discontinuance of the system.

I believe this experience has been confirmed by other iron-masters in furnaces having a still larger capacity than 25,500 cubic feet (43,000 cubic feet), and, in some instances, where the height was 95 feet instead of 80 feet.

It cannot be denied that the operation of calcining ironstone is one requiring heat, for we have solid water and solid carbonic acid to transform into vapour, to set against which there is the heat due to the fixation of half an equivalent of O, by reason of the Fe O passing into the state $Fe_2 O_3$.

In practice, this heat is measured by the quantity evolved by the combustion of ·66 cwt. of coal for each ton of ironstone. The number of heat units evolved from such coal as is employed, according to the data formerly given, may be taken at 8,000 calories per unit. From this we may take the quantity of heat evolved by ·66 cwt. coal as equivalent to 5,280 units.

Now, if there is any economy of fuel to be effected by the substitution of raw for calcined stone, it must result either from a profitable absorption of heat now wasted, or there must be some change of a beneficial nature, chemically speaking, by expelling the CO_2 and H_2O in the neutral or deoxidizing atmosphere of the furnace, instead of in the kiln, where, from the nature of the operation, the iron becomes permanently peroxidised.

On referring to the Section (XXVIII.), on the quantity of heat required in the process of iron smelting, it will be admitted that the only source which can afford any relief in the matter of direct absorption, is the sensible heat in the waste gases. According to the views laid down in Section XXXII., it was deemed impracticable, when using calcined stone, to reduce the loss from this cause, owing to the chemical and heat developing action in operation, near the top of the furnace. It by no means, however, follows that to some extent this escaping heat might not be usefully employed by introducing a heat absorbing action, such as expelling carbonic acid and water from ironstone, provided the temperature of the gases is sufficient for the purpose.

Exp. 715. By the kind permission of the proprietors of the Normanby Works, I ascertained, during five hours, the tempera-

tures of the gases as they left the furnaces using raw stone in the proportion formerly mentioned, *i.e.*, one-third of the iron was from uncalcined ore. One experiment gave a mean temperature of 320°C. (608°F.), and another 269°C. (516°F.)

During these observations charging was continuous, so that the great rise of temperature, which takes place during its cessation at meal times, is excluded. Making allowance for this, it will be probably pretty near the mark if it is assumed that the gases from these two furnaces left them at an average of 55°C. (100 F.) lower than those when calcined stone and raw limestone are employed.*

The gases per ton of iron would weigh somewhat more when raw ironstone is used; calling it 130 cwts., and the reduction of temperature 55°C., we have (130 cwts. × 55° × ·24 sp. heat) 1,716 cwts. heat units intercepted from the cooling effect of using 20 cwts. of unroasted stone per ton of iron. These figures do not correspond with the heat I have considered as actually absorbed in the mine kiln. The number obtained there was 5,280 calories, which makes it look as if there was still a considerable loss in the calcining kiln.

The use of a portion of the ironstone in its unroasted condition at the Normanby Works having been accompanied by employing the whole of the flux in the form of caustic lime, the actual nature of the results obtained at this establishment will be taken up again at the close of the present section, after the subject of calcining the limestone has been considered.

As a commercial question, this use of raw stone is scarcely worth considering at greater length, inasmuch as it has not been found, under the most favourable circumstances, practicable to use above one-third in this unprepared form, owing, no doubt, to the escaping gases being cooled below the point required for expelling the CO_2. The saving is, therefore, too small to risk the inconvenience experienced by most manufacturers who have tried it. As a matter of scientific interest, however, I will give the particulars of a few trials made in connection with the properties of raw ironstone.

Exp. 716. A quantity of calcined Cleveland stone, the size of mustard seed, was placed in a combustion tube, and heated to the

* Upon two occasions, exclusive of the dinner hour, the gases were found to leave the Clarence furnaces of 25,500 cubic feet at 650 and 700 F. respectively (343°C. and 371°C).

temperature of softened zinc, possibly 410°C. (770 F.), all air being previously expelled. A stream of CO freed from CO_2, O, and H_2O by SO_4 H_2, KHO, and pyrogallic acid was conducted over it for 3½ hours.

Loss of weight, after operation	2·55	per cent.
C found in residue ...	·90	„
Total loss, consisting of oxygen	3·45	„
3·45 O corresponds to ... ... CO_2 ...		9·5
·90 C (from action $2CO = C + CO_2$) $= CO_2$ ...		3·3
		12·8

The total quantity of CO_2 collected while passing CO over the ore was 13 per cent.

It is worthy of notice that of the total CO_2 collected, just about one-fourth is due to the reaction $2\,CO = C + CO_2$, or for each equivalent of CO_2 resulting from this reduction three proceed from the reduction of the Fe_2 O_3.

Exp. 717, of precisely the same nature as the previous one, was performed on unroasted Cleveland stone, precautions being taken to collect the combined H_2O, by means of Ca Cl_2. The specimen only contained 15 per cent. of CO_2.

CO_2 originally in the ironstone ...	15·	per cent.
After experiment	4·4	„
CO_2 expelled	10·6	„
H_2O do.	7·9	„
CO_2 and H_2O	18·5	„
Total loss of weight	20·0	„
Difference	1·5	„
Carbon found in residue	1·7	„
Net difference, consisting of oxygen	3·2	„
3·2 of oxygen corresponds to CO_2 ...	8·8	„
Weight of CO_2 expelled was ...	10·6	„
1·7 C from action $2\,CO = C + CO_2 = CO_2$	6·2	„
	25·6	„
Total quantity of CO_2 directly observed	23·3	„

It would appear, from these two experiments, that using the raw stone does not interfere in any way with deoxidation; for although there was a greater percentage of oxygen in the first trial (the metal being all as $Fe_2 O_3$), the actual loss of this element is nearly the same in both cases, viz., 3·45 and 3·2 per 100 of substance operated on. As regards carbon impregnation, the raw stone contained near double that of the calcined, and, reckoned upon the Fe present, the 2·14 was found in the roasted ore, against 5·31 in the raw.

In Section XI. instances were quoted of similar results being obtained on exposing raw and calcined Cleveland ironstone in the escaping gases of a blast furnace, 100 Fe present taking up in 24 hours 4·63 in the first, against 1·68 in the other.

In the division of this work just referred to, I suggested the possibility of the change which $Fe CO_3$, as it exists in Cleveland stone, experiences on being heated, might be the cause of the appearance of this additional C, when the ore was employed raw.

Exp. 718. A quantity (300 grs.) of raw stone was placed in a green glass tube, and heated to dull redness, until no more volatile matter was given off. The ore lost, in about 30 minutes, 23·3 per cent., and contained ·37 of C, a much less quantity than that named in the previous experiments; but this might in a great measure be due to the temperature being such as to enable the deposited C to be carried off, or to the fact of the experiment being concluded in a much shorter time than those numbered 716 and 717.

One advantage looked for in exposing raw ironstone ($Fe CO_3$) to calcination, where the iron could not pass into the state of $Fe_2 O_3$, was by avoiding peroxidization of the metal to save the work in the blast furnace. I will presently show that it is a fallacy to hope for any economy of heat in deoxidizing Fe O rather than $Fe_2 O_3$; but, were it otherwise, the expectations of those who look for profit in this way could not be realized, for the simple reason that under no circumstances have I found Fe O to result from the roasting of $Fe CO_3$, even where all access of air was excluded.

In Exp. 236,* on examining the oxide left on calcining raw Cleveland stone at a full red heat in a current of pure N, the Fe O

* The temperature is given in Sec. XI. erroneously as 200 C. The ore was dried at this heat, but afterwards exposed in the current of N to a full red.

had been converted into Fe_2O_3, and in which it was considered the reaction must have been—

$$2\ Fe\ CO_3 = Fe_2\ O_3 + CO + CO_2.$$

Exp. 719. When spathose carbonate was similarly treated, the iron was obtained as magnetic oxide, and apparently, therefore, the change had been as follows :—

$$3\ Fe\ CO_3 = Fe_3\ O_4 + CO + 2\ CO_2.$$

The nature of the reaction, however, apparently is modified by the temperature to which the ironstone is exposed.

Exp. 720. A specimen of well-dried raw stone was exposed to a low red, air being excluded, until it ceased to give off any more gas: the loss was equal to 23·3 per cent., which is almost exactly that where Cleveland stone is calcined in contact with O. It would, therefore, appear the Fe was peroxidized, but the gas emitted contained CO_2 and CO in the proportion of 8 vols. of the former to 1 of the latter. The residue contained ·37 per cent. of deposited carbon.

It having been ascertained that raw ironstone, exposed to heat, and, when protected from oxidizing influences, becomes more readily impregnated with carbon than calcined stone similarly treated, it might be supposed this would lead to a saving of fuel. This, however, will be found in practice not to happen; because in a furnace sufficiently large to work at a maximum of effect, the gases are already charged with as much CO_2 as they will carry; and as carbon impregnation is accompanied by a simultaneous generation of CO_2, the production of free carbon from this source is either arrested, or if not arrested, a corresponding equivalent of deposited C, or of the carbonaceous constituent of the coke is dissolved.

Everything considered, it would seem there is no alternative left but to conclude that in no case can there be a saving of heat by the use of raw stone beyond that abstracted from the escaping gases. These, upon the occasion of using one-third of the ore uncalcined, had only given up about one-sixth of their sensible heat; and the reason, probably, why the use of more than this quantity of stone in the unroasted state seriously affects the condition of the furnace will be an evolution of CO_2, at a point where the temperature is such as to lead to the reaction of this on the carbon.

An anticipated objection to the introduction of raw stone was a supposed reduction in the combustibility of the escaping gases by the addition of so much more CO_2, thereby depriving them of their useful application for raising steam, and heating the blast. If, as it has been suggested, the carbonic acid leaves the ironstone partly as CO, the 4·4 cwts. CO_2 contained in the 20 cwts. of raw ironstone cannot materially affect the value of the escaping gases. Mr. Jones obligingly favoured me with two analyses, made by Mr. Bowron, of Stockton, of the gases from two furnaces, one working with both limestone and ironstone calcined, and the other with limestone and different proportions of the ironstone, also calcined, and the remainder of both limestone and ironstone were all raw.

	Exp. 721. Ironstone and Limestone, both Calcined.	Exp. 722. Limestone Calcined. 25 % Ironstone Raw.	Exp. 723. Limestone Calcined. 37 % Ironstone Raw.	Exp. 724. Limestone and Ironstone Raw.
N ...	50·79	52·14	51·63	50·73
CO ..	28·90	29·14	27·80	27·90
CO_2 ...	15·07	13·68	16·35	16·15
H ...	1·45	1·05	·50	·95
Hydrocarbons	—	·56	—	tr.
H_2O ...	2·82	2·83	3·00	3·62
Fume ...	·97	·60	·72	·65
By weight	100·	100·	100·	100·
100 by weight of $CO=CO_2$	52	47	59	57·3

None of these examples, it must be remarked, are very rich in CO_2, 62½ to 100 of CO not being an uncommon proportion at other works. It may further be remarked that it is not improbable that the CO_2 may be overstated in the analyses of the Normanby gases just given here, inasmuch as the specimens of gas were collected during the dinner hour, and would not, therefore, fairly represent their average composition. Upon such occasions it is by no means uncommon for the CO_2 to increase as the temperature of the gases rises, and those portions of the coke which are most capable of being removed by the solvent power of this dioxide of carbon, having been already carried off, there is, for some time at all events, nothing to restrain the formation of CO_2, and in consequence it goes on increasing.

At the Wear furnace (80 feet high, 17,500 cubic feet), using calcined ironstone and raw limestone, the average composition of 14 specimens of the escaping gases was as follows:—

		By Volume.	By Weight.
Exp. 725.	N	59·96	58·00
	CO	27·53	26·63
	CO_2	10·00	15·20
	H	2·51	·17
		100·	100·
	100 CO = CO_2	36·3	57

When using raw stone, the average of 8 samples of the escaping gases gave:—

		By Volume.	By Weight.
Exp. 726.	N	58·9	57·6
	CO	30·3	29·6
	CO_2	8·2	12·6
	H	2·6	·2
		100·	100·
	100 CO = CO_2	27·	42·5

The attempt to use the ironstone in an uncalcined state was unsuccessful at this furnace. The iron fell considerably in quality, as may be inferred from the composition of the gases; for it will be observed that not only has the whole of the CO_2, introduced by the raw ore, been reduced to CO, but one-fourth of that due to the deoxidation of the iron oxide has shared the same fate.

Neither experience nor reasoning, founded upon the known action of the smelting process, justifies the belief that more than a small proportion of the ironstone, unprepared by roasting, can be admitted into the blast furnace. Under such circumstances, it is desirable to consider what are the conditions to be aimed at in this preliminary treatment of the ore before it reaches the hands of the smelter.

In the best of kilns, too active combustion, produced either by the accidental use of too much fuel, or by winds, affords the calcined ironstone occasionally in a fritted, or almost fused state, when, instead of being of a brick-red colour, and open in texture, it is almost black, close grained, and very hard.

The reducing action of the gases has been described as being effected by the CO penetrating the interstices of the ironstone exposed to its influence. It is clear, therefore, that if, instead of being highly porous as red burnt ironstone is, it is the very reverse, this penetrability must be greatly impaired, and deoxidation retarded.

In illustration of this, different samples of Cleveland stone, varying in the manner in which they were calcined, were experimented upon. They consisted of—

No. I. Cleveland stone, soft and porous; colour, brick red.
„ II. do. harder than No. I., not fritted; colour, brown.
„ III. do. still harder than No. II., slightly fritted; dark purple.
„ IV. do. partially fused; black.
„ V. do. fused; resembled mill cinder.
„ VI. Lancashire; rich kidney ore.
„ VII. Elba; specular ore, dense.

These seven specimens, broken to the size of mustard seed, were placed in capsules, and exposed to the reducing gas in the lead bath arrangement:—

Exposed 8 hours to CO	Exp. 727.	Exp. 728.	Exp. 729.	Exp. 730.	Exp. 731.	Exp. 732.	Exp. 733.
Zinc softened.	No. I.	No. II.	No. III.	No. IV.	No. V.	No. VI.	No. VII.
% original O removed ...	56·1	65·2	52·6	30·4	23·9	67·70	51·7
C per 100 Fe deposited ...	5·6	21·5	8·8	1·5	·51	54·3	26·

All the Cleveland samples were taken from the same block of ironstone, but differing in degree of calcination; other specimens were then broken off different blocks, corresponding as nearly as possible with the above numbers, and tried as follows:—

Exposed 8½ hours to CO / Zinc softened.	Exp. 734. A	Exp. 735. B	Exp. 736. C	Exp. 737. D	Exp. 738. No. VI.	Exp. 739. No. VII.
% original O removed ...	54·	49·3	49·	40·2	68·4	47·8
C per 100 Fe deposited ...	1·2	—	—	—	139·6	36·3

In this case, A was collected to resemble No. I. in Exp. 727.
B „ „ II. „ 728.
C „ „ IV. „ 730.
D „ „ V. „ 731.

but there was a slight difference between the specimens lettered and numbered. Exps. 738 and 739 were Lancashire and Elba ore, the same as in Exps. 732 and 733.

The scoria obtained from the rolling mill furnace, a silicate of iron, is very dense, and very impenetrable by any gaseous substance.

Exp. 740. A quantity, the size of millet seed, was placed in a tube, and exposed during 3½ hours to the highest temperature of a single Hofman's furnace. It only parted with 1·35 per cent. of its oxygen, and contained no deposited carbon.

Exp. 741. Another specimen was placed in the escaping gases of a 48 feet furnace. In 48 hours it only lost about 16 per cent. of its oxygen, and contained about ·25 of C per 100 of Fe.

Exp. 742. A specimen of calcined Cleveland stone, exposed in the escape-pipe of the same furnace, during the same period as Exp. 741, lost 52·3 per cent. of its original oxygen, and contained 2·42 of C per 100 of Fe.

Having, as I believe, disposed of the question of the possibility of using clay ironstone to any great extent in its raw state, and of there being any economy worth the name in employing the small quantity which is practicable, I would now ask attention to another change which has been advocated* of an entirely opposite character, viz., the complete deoxidation of the $Fe_2 O_3$ before it is delivered to the blast furnace, whose duty will then be restricted, it is expected, to fuse the metal and slag.

The following are the reasons why this over-preparation, as it were, offers little chance of success, in which respect it is inferior to the idea of using raw stone, a portion of which latter, at all events, may be employed without loss.

Whatever measure of relief which may be afforded to the work to be performed in the upper zone of the furnace, it is clear we must have at our command sufficient heat to effect that part of the operation which is carried on in its other portions. Now, the only relief which this deoxidation of the ore can place within our power is that absorbed by the gasification of its oxygen.

If we turn to Section XXVIII. the enumeration of heat units

* Transactions of Mechanical Engineers, 1870.

required for the entire process of smelting the Cleveland stone is stated to be, in round numbers, as follows:—

No. 1. For fusion, radiation, &c.; in short, every stage, except reduction, carbon impregnation, and loss in the escaping gases, ...	50,000	cwt. heat units
No. 2. For reduction and carbon impregnation, ...	34,500	„
No. 3. For loss in the escaping gases, ...	9,000	„
Total	93,500	„

If, instead of delivering $Fe_2 O_3$ to the furnace, we have to deal with spongy iron already impregnated with carbon, the cwt. heat units set down against these items will not be needed. Probably, also, as there will be a suppression in a great measure of chemical action near the top of the furnace, there will be diminution of heat contained in the escaping gases. Calling this diminution 2,000, it leaves 57,000 cwt. heat units required for the divisions distinguished as Nos. 1 and 3.*

There being under this altered state of affairs no reduction, it may be assumed there will be little or no CO_2 in the escaping gases; hence the heat evolved from the coke will be that obtained from its combustion in the hearth (C to CO) *plus* the heat contained in the blast.

According to the data contained in the Section just referred to, the coke and blast afforded almost exactly 57,000 cwt. heat units,† so that there is not any margin of actual heat to be saved by the

---

* Total heat required as above	93,500	units.
Less 2,000 less in escaping gases	2,000	„
	91,500	„
Heat for reduction and carbon impregnation no longer required	34,500	„
	57,000	„
† C burnt to CO	45,024	units.
Blast contained	11,919	„
	56,943	„

change. It could not indeed be otherwise, seeing that the process of reduction of Fe_2O_3 by CO has been shown not to be one of a heat absorbing, but rather one of a contrary character.

It has been already explained that the barrier to the substitution, beyond certain limits, of blast heat for coke heat, was the necessity of retaining, at the various temperatures of the furnace, a deoxidizing atmosphere; and that this condition was interfered with by the appearance of what, under the circumstances, was an excess of CO_2, which excess was carried off by $CO_2 + C = 2\,CO$, which means waste of coke. If, however, the nature of the process going on in the interior of the furnace was such that no CO_2 was formed, it is quite obvious that the objection to the substitution of heat in the blast for that obtained by burning coke, disappears.

To be sure of this, we must assume, which it is perhaps too much to do, that the deoxidation proved to be effected near the tuyeres can be carried on with that reduced quantity of CO, compared with the iron made, which inevitably follows any diminution in the quantity of coke consumed.

Granting, however, the freedom from all difficulty on this score, in order to reduce the consumption of coke 4 cwt. per ton of iron the blast would have to be raised to about 800° C. (1472° F.) to contain as much heat as that lost by the suppression of this quantity of fuel. I have adopted the saving of 4 cwt. of coke as the basis of calculation, because 800° C. is generally admitted to be the maximum temperature which can be commanded by the fire-brick stoves, and hence it may be regarded as the practical limit to be gained by the total absence of CO_2, resulting from the reduction of $Fe_2\,O_3$.

The next matter for enquiry is the actual cost in heat of the operation of reduction, as it is at present performed in the blast furnace, and the answer has already been given in this work. The gases rising from the hearth part with their heat to the descending column of materials, and leave a furnace, say of 80 feet, very much cooled, but still containing warmth enough to raise the temperature of the incoming ironstone to that point where reduction readily begins, viz., at a temperature of about 345°C. (653°F.) Once started, the operation continues, accelerated by the increasing temperature of the furnace as the ironstone descends, and the heat is further somewhat augmented by the action of reduction itself

In such a furnace as that mentioned, almost the full equivalent of CO_2 due to reduction and carbon impregnation escapes as such, and the consequence is, we have (*v.* Section XXVIII.), 36,512 units developed by the generation of CO_2 to supply 34,548, the sum of the absorption which takes place from reduction of Fe_2O_3 to Fe, or an actual gain of almost 2,000 units.

If, then, there has to be any advantage by the use of ore already deoxidized, it must be by the substitution of superheated air for coke in the manner already described, and not by any actual economy of heat.

The proposition is, to effect the deoxidation of the ore by the gases escaping from the blast furnace itself. Now, it must not be forgotten that we are supposed to have economized our coke to the extent of 4 cwt. per ton of iron, hence we begin the operation with something like 9 cwt. less CO than is present in the actual mode of conducting it, *i.e.*, there will be about 35 cwt. instead of about 44 cwt. of gas.

The first demand upon our resources will be to reinstate the gases in their former position in respect to temperature, in order that the process of deoxidation may commence as soon as the raw ironstone is prepared for its initiation. For this they will probably require at least the 2,000 units of heat per ton of iron restored to them which were supposed to be saved by depriving them more thoroughly of their sensible heat, along with, say 2,000 calories more, which they will have parted with during their conveyance from the blast furnace to the apparatus in which the raw ironstone has to receive its preliminary preparation. Looking at the quantity of heat apparently required to calcine 20 cwt. of ironstone in the blast furnace, we cannot take less than ($3\frac{1}{4}$ tons × 1,716) 5,577 heat units for expelling the CO_2 and H_2O. Thus, the gases which have to effect this operation have to be loaded with (2,000 + 2,000 + 5,577) 9,577 units before deoxidation of the raw ironstone can commence; and, as each unit of CO gives 2,400 heat units by its combustion into CO_2, we have 9,577 ÷ 2,400, or close on 4 cwt. of our 35 cwt. of CO absorbed for this work, reducing it to 31 cwt.

Taking the gases leaving an 80-feet furnace as given in Section XXVIII. as the basis of calculation, the composition, after they have reduced the raw ironstone, will be as follows:—

4·00 CO burnt to CO_2 to obtain necessary heat for calcining the raw stone per ton of iron		= 6·28	cwt. CO_2
6·52 C as CO, say 15·21 cwt. CO burnt to CO_2, for reduction and carbon impregnation, ...		23·91	
CO_2 emitted by 65 cwt. ironstone during calcination (say half its C as CO and half as CO_2), ...		7·15	
Total CO_2 in reducing apparatus, ...		37·34	cwt. CO_2
31 cwt. of CO, diminished by 15·21, being converted into CO_2. 31—15·21=	15·79		
One-half of C in ironstone emitted as CO,	4.55		
		20·34	cwt. CO
		57·68	

In such a mixture, the proportion of CO_2 per hundred of CO is 183. Here, it will be observed, we are landed in a much greater difficulty than that which limits the reducing power of the gases in the furnace itself, viz., the presence of so large a quantity of CO_2 as to convert them, if so changed, into a powerful oxidizing medium.

If, as I understand, the CO used for calcining is to be heated in a Siemens regenerator, 6·28 cwt. of the above CO_2 will be removed from the atmosphere in the reducing apparatus, but this would still leave the proportion of CO_2 to CO as 153 to 100, which is quite inadmissible.

In the preceding statement, no account is taken of the fuel to be spent in rising the temperature of the air to the 800°C. spoken of—nor will it, after what has been laid down, be deemed necessary to point out in detail, the additional apparatus which will be required for this purpose, as well as that for heating the gases before they are admitted to the ironstone, and the chambers in which the ironstone has to be deoxidized. This portion of the plant would be very extensive, and necessarily the reduced iron would have to be immediately transferred to the furnace, otherwise it would incur great risk of absorbing O on coming in contact with the air before it was cooled—an act which means loss of heat and waste of fuel.

I would just add a word respecting the deoxidized ore itself. In all probability, from the bursting up of the ore by the act of

carbon impregnation, it would be obtained in a state of considerable disintegration, through which the blast would pass with extreme difficulty; and this preliminary reduction might, it is just possible, be attended with another inconvenience, suggested by the recent experience of Mr. Ferrie, who kindly communicated the same to me.

Into his self-coking furnace he introduced a small proportion of the ironstone in its raw state. This, being black band, contained a certain quantity of coaly matter, which, acting rapidly on the iron oxide at the upper part of the furnace, completely reduced it, probably before carbon impregnation from the dissociation of CO had broken it up, and deposited C in that form readily absorbed by the metal, so as to constitute cast iron. At all events, whatever the cause, masses of matter came down to the tuyeres, and so impeded the work, that the blast had to be taken off, and the obstruction removed, which was found to be malleable iron in so perfect a form, that it was taken to the mill, heated in an ordinary balling furnace, and rolled out into a bar.

LIMESTONE.—The use of carbonate of lime as a flux in the blast furnace is attended with a two-fold expenditure of heat. There is, firstly, the direct absorption by the escape of its CO_2; and, secondly, this CO_2, so liberated, carries off a quantity of carbon equal to its own by the action $CO_2 + C = 2\ CO$.

The usual quantity of limestone employed in smelting the Cleveland stone is about 11 cwt., and the following statement sets forth the number of heat units absorbed:—

Expulsion of CO_2, from 11 cwt. × 370 heat units,	4,070
1·32 C in Ca CO_3 carries off equal weight of C, which, not arriving in the hearth, where, oxidized by hot air, it would yield about 3,000 units, 1·32 × 3,000, ...	3,960
	8,030

Some economy in point of expense can be effected in burning the limestone before it is taken to the blast furnace, because the fuel, small coal, is only about one-fourth the price of coke. Unfortunately, however, this saving only applies to the first of the items named above, and apparently for the following reason:—

In the cooler part of the furnace the existence of CO_2 is only an

evil so far as it impairs the activity of the reducing agent, CO, the heat being insufficient to enable the C to abstract any of the O of the CO_2.

Exp. 742. It was found when quicklime was exposed at a red heat to a current of CO_2, it absorbed in a few hours one-third of the CO_2 required to convert it into Ca CO_3. There will, doubtless, be by this means an evolution of heat equal to 370 units per unit of Ca CO_3 formed, but this will take place so near the top of the furnace that it is not unlikely a portion will be carried off in the escaping gases. On the other hand, the CO_2, withdrawn from the gases where it is harmless, will be carried down and expelled under the same conditions as if so much carbonate of lime had been used, *i.e.*, the CO_2 will dissolve its equivalent of C.

On referring to the tables and diagrams given in Section XXXIV., it will be found the escaping gases agree, of course, with the change made in the state of the flux; and, although it is difficult to institute a very rigid comparison between the composition lower down, owing to the possibly varying amount of dissociation of CO, by which C is precipitated, there is litttle doubt that no material alteration has taken place in the quantity of C and O, at a point 12 or 15 feet from the top. From this I infer that the caustic lime has absorbed a large quantity of CO_2, and brought it down to a level where this acid is resolved into CO.

This will, to some extent, account for the observed fact that the economy of fuel in employing calcined limestone never quite amounts to that of the actual quantity required for burning it, affording thus a confirmatory proof that the loss resulting from the reaction of the liberated CO_2 on C remains unchanged.

Admitting that by the use of limestone, calcined so as to contain no trace of CO_2, the saving of heat in the furnace using CaO equal to that contained in 11 cwt. of Ca CO_3 would be 11 × 370 calories = 4,070 units, the absorption of heat by employing 20 cwt. of ironstone per ton of metal in its raw state would be somewhere between 1,716 and 5,000 units, according as the heat taken from the gases, or the consumption of coal in the kilns is taken as the standard. If we take it at the mean of these two numbers, we have 3,350, of which 1,716 is obtained from the gases themselves, leaving 1,600 to be provided from the usual heat resources of the furnace.

Applying these figures to the work performed at the Normanby Works when the flux is calcined, and 20 cwt. of ironstone per ton of metal is used raw, we have, as compared with a furnace using all calcined ironstone, and its limestone raw, 4,070 units saved by the use of caustic lime, and 1,600 expended by using a portion of its ironstone raw, leaving a net gain of 2,470. These furnaces, Mr. Jones informs us in a recent paper, made, during a period of six months, one ton of iron, of a quality close on No. 4, with a trifle above 20·75 cwt. of coke. The quantity of heat required for No. 4 iron is less than No. 3. I have, in the preceding Section, given my reasons for considering it to be about 1,200 units; so that, to institute a parallel between the Normanby furnaces, and one of those at Clarence, using calcined ore and raw limestone, making No. 3 iron, we should have to add (2,470 + 1,200) 3,670 units, which will bring up the coke consumption to about 22 cwts. per ton of iron. As a rule, it may be observed, the Normanby furnaces are working on forge iron, whereas at the Clarence Works a large proportion of foundry metal is constantly being aimed at. I have already shown how these different modes of working may give a slight advantage to a furnace burdened for the lower quality of iron.

On the whole, therefore, it appears to me, the two furnaces working raw stone at Normanby are doing very good work; but, so far as actual economy in heat is concerned, the only credit they are entitled to is the 1,716 calories they take from the gases, over and above that usually obtained from furnaces working roasted stone. Looking at the composition of their gases, this may be taken as representing half a cwt. of coke, more or less.

SECTION XXXIX.—ON THE THEORY OF THE HOT BLAST.

In the year 1828, J.B. Neilson patented an "improved application of air to produce heat in fires, forges, and furnaces, where bellows or other blowing apparatus are required." This discovery consisted, as is well known, in heating the air before it is propelled into the furnace; and although, from the title of the patent, Neilson and his colleagues appear to have expected to see it generally employed in all furnaces driven by compressed air, its use has, practically, been exclusively confined to those employed in smelting the ores of iron.

In 1834, Monsieur Dufrenoy was sent over to this country, by the Director-General of Mines of France, to report to the authorities at Paris, on an invention, which at the time was truly described as one revolutionising, in Scotland at all events, where it was first put into practice, the art of making iron.

This gentleman in a report* gave good reasons apparently for this statement, by quoting the experience of the owners of the Clyde Iron Works, which was as follows:—

For the year Temp. of blast Coal used per ton of iron	1829. Cold. As coke.	1831. 450° F. As coke.	1833. 612° F. In raw state.
For fusion, cwts. ...	133	86	40
„ heating air, raw coal	nil.	5	8
„ blowing engines „	20	7	11
	153	98	59
Cwts. limestone per ton of iron	10½	9	7

* "On the use of hot air in the ironworks of England and Scotland;" translated 1836. London: J. Murray, Albemarle Street.

From this it would appear that heating the air with 5 cwts. of coal had saved 47 cwts. of fuel in the furnace, and 8 cwts. similarly applied had been followed with an economy of 93 cwts., or above 69 per cent.

Besides this advantage, the make was increased by more than one-third, and a blowing engine, which only supplied three furnaces with cold blast, was equal to four when the air was heated.

The iron trade hesitated somewhat in crediting that the heat generated from 8 cwts. of fuel burnt outside the furnace should be able to perform the duty of a very much larger weight burnt inside. Some writers on the metallurgy of iron, when speaking of the advantages of Neilson's system, have perhaps not been sufficiently careful in drawing a distinction between the saving directly due to its application and that arising in a collateral manner from its use. Looking at the question, however, in its commercial sense, the figures and language quoted from the work of Dufrenoy justified the character he gave of it.

There is undoubtedly, as this writer alleged, a saving, and, in the case of the Scotch furnaces, a very great saving, of fuel by the use of the hot blast, exceeding considerably that of the weight of coal expended in the hot-air apparatus; but it seems a mere waste of time to endeavour to assign a cause, *in a heat-producing point of view*, why with the blast at 450°F., obtained by burning 5 cwts. of coal, 93 cwts. of fuel should do the work of 153 cwts. with cold air, for the simple reason that it is incorrect so to state the economy effected by the invention. Thus, the burning of 7 cwts. instead of 20 cwts. of coal, per ton of iron, under the blast engine boilers does not affect beneficially the quantity, nor the application, of the heat developed in the furnace itself.

Again, according to Dufrenoy, the coal used at the Clyde Works contains 64·4 per cent. of coke; but in the statements of the consumption he gives, there was used, per ton of metal, at the furnace blown with—

					Raw coal.	
Cold blast, ...	60	cwts.	of coke,	obtained from	133	cwts.
Hot blast, 450°F.	38	„	„	„	96	„
Difference	22	„	„	Difference	37	„

These quantities of coke, viz., 60 and 38 cwts., in reality only represent 93 and 58 cwts. respectively of raw coal, the difference between these numbers and those quoted above being waste of fixed carbon in the coking process. Hence, although it may be perfectly correct, commercially speaking, to say there is a gain of 37 cwts. of coal, in a heat-producing point of view, it is only 22 cwts. of coke we have to set against 5 cwts. of coal burnt in the hot-air stoves. This margin of 17 cwts. (the difference between 22 and 5 cwts.), however, is sufficiently remarkable, and various explanations have been given to account for the apparent anomaly. Some of these I propose to examine in the present section, and then to consider the question with the assistance of the experiments and reasoning made use of in my own investigations on the action of the blast furnace.

The late Dr. W. Allen Miller* conceived the economy effected by the use of the hot blast to be due to the reduction of the ore taking place nearer the crucible, and thus concentrating the heat.

The analyses of the gases at different depths of the furnace, quoted in these pages, when blown with cold air, and with that varying from 180°C. to near 500°C., do not appear to afford any countenance to the opinion advanced by this chemist.

Dr. Clark, Professor of Chemistry in Aberdeen, examined, in 1834, the action of the hot blast, and assigned as the cause of the saving of fuel that an ordinary furnace received six tons of cold air per hour, which he regarded as a tremendous refrigeratory passing through its hottest part, and thus repressing the temperature required for the complete and rapid reduction of the iron.

This explanation of the cooling effect of the air is true enough, but it scarcely accounts for the fact that one unit of heat in the blast was at that time saving something like four derived from the fuel burnt in the furnace. Dr. Clark, too, appears to have entertained the same opinion as that expressed some thirty years afterwards by Dr. Miller, viz., that the reduction of the iron was an operation performed in the hottest part of the furnace, whereas it would seem, from the analyses given in a previous part of this work, it is one almost exclusively effected in the coolest region.

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* "Elements of Chemistry."

Mr. Truran, in his work,* maintained that all writers previous to his time had greatly exaggerated the effects of the hot blast in the manufacture of iron. Dr. Percy† has effectually disposed of the chemical reasoning upon which this author supported his assertion. I am not aware that any one pretended that its introduction into Wales had been attended with the same beneficial results which distinguished its use in Scotland, and Mr. Truran certainly did not succeed in proving that Neilson had not, by his invention, afforded very valuable assistance in smelting the black-band of that country.

Sir Wm. Fairbairn, in his work on the manufacture of iron, suggests the propriety of investigating the alleged consumption of fuel in the throat of the furnace, to which Mr. Truran attributed certain effects of the hot blast. Sir William himself seems to be under the impression that narrowing the throat increases the effect of the blast in this region. As no portion of the blast ever reaches beyond a few inches from the tuyeres in the form of atmospheric air, whether it is employed hot or cold, and whatever be the shape of the furnace, this view of a change in the nature of the combustion seems also devoid of any foundation.

Dr. Percy, who has examined with great care and minuteness the writings of almost every author, English and foreign, on this question, states‡ that, "after the positive, oft-repeated, and generally credited statements which have been put forth concerning the extraordinary effect of the hot blast in diminishing the consumption of fuel in the smelting of iron, it might seem superfluous to raise any question as to the fact."

The extraordinary effect alluded to by this author would appear to have more special reference to such savings as are contained in the published accounts of the late David Mushet, who gives 148 cwts. of coal coked for making a ton of iron with cold air, against 43½ cwts., used raw, with hot air, at the Clyde Works.

Dr. Percy considers that the abstraction of heat by the expansion of so much cold air when it enters the tuyeres must, by the mere act of dilatation, produce an unfavourable effect on the condition of the furnace, and that heated oxygen, combining more rapidly

* "Iron Manufactures of Great Britain," 1855.

† "Metallurgy of Iron and Steel."

‡ "Metallurgy of Iron and Steel," p. 418.

with incandescent carbon, will give a temperature of greater intensity in the direct ratio of rapidity of combustion. This being so, he adopts, for the sake of argument, the supposition that a metal requiring 1,000°C. for its fusion might be subjected to a temperature of 999°C. forever without melting. So it may be, the Doctor continues, in the blast furnace, with respect to the carburization of the reduced iron, and certain other accompanying chemical actions, which may take place with slowness at one temperature, and with rapidity at another, slightly elevated. In order to produce these actions in a furnace on cold blast, it is requisite to consume a much larger quantity of coal than in a furnace on hot blast. A few degrees of temperature may make all the difference. As a further proof that it is *calorific intensity* which constitutes the superiority of the hot over the cold blast furnace, Dr. Percy mentions that in both cases the fuel is wholly consumed, and as the gas also which escapes from the furnace mouth has substantially the same composition, it follows that the *amount* of heat generated in a furnace working with cold blast is enormously greater for a given weight of pig iron than in one working with hot blast, the conditions with respect to quality of ore and fuel, dimensions of the furnace, &c., being supposed to be the same in both cases.

A word or two with regard to the absorption of heat by expansion as the blast enters the furnace, and the identity of the composition of gases from hot and cold blast furnaces.

Admitting that a current of cold air absorbs more heat by its expansion than one of hot air, both having the same pressure, will this absorption, whatever it may be, not be met by the addition of precisely the same quantity of heat if communicated to the blast itself? If so, we are not called upon to explain, so far as this item is concerned, any discrepancy between the heat communicated to the air, and the actual effect it produces in the furnace; for there would be no difference between the two. As regards the composition of the gases, it is difficult to determine, from mere reasoning, what this would be. The action of the blast on the fuel would undoubtedly, in both cases, give CO; and the actual quantity of CO_2 produced by reduction and carbon impregnation would be the same in the hot as in the cold blast furnaces, but what proportion of this CO_2 might suffer reduction to the state of CO is not so clear, but supposing it also were the same in both

furnaces, inasmuch as the cold blast furnace is burning much more C to the condition of CO, and cannot convert more of this CO to CO_2 than happens when heated air is used, it follows that it is highly improbable that Dr. Percy's prediction as to their identity of composition would be realised.

Dufrenoy gives it as his opinion that the virtue of the hot blast is to be ascribed to the higher temperature of the furnace, and in support of this hypothesis, he adduces the fact that less limestone is used than when working with cold air, and hence "this diminution of the fluxing matter is the strongest proof that can be given of the temperature of the furnace. It proves that the earthy particles undergo a degree of heat powerful enough to fuse them, with the addition of a smaller quantity of flux."

This view of the condition of the zone of fusion is also that entertained by Dr. Percy, who reminds us that in looking into the tuyere of a cold blast furnace, the interior is black, instead of presenting the dazzling bright appearance of one blown with heated air.

As regards the diminution of limestone, there are other objects to be gained than the mere fluxing of the earthy constituents of the ironstone, such as the removal of sulphur, &c. This would appear to be so, because it often happens that the earths, in the proportions in which they exist naturally in an ore, constitute a readily fusible slag without the addition of any flux; thus, according to Colquhoun, in Scotch Black Band, we have them as follows:—

$Si\,O_2$ 38, $Al_2\,O_3$ 21, Mg O 18, Ca O 23=100.

Exp. 743. A mixture of these four substances in the specified quantities was exposed to the heat of a smith's forge, when it melted readily into a vitreous slag; and similarly, when they were in the proportions in which they are found associated in the Cleveland ironstone, they afforded a beautiful white glass.

The supposed duty of lime in removing sulphur, and it may be phosphorus to some slight extent, often leads to its use where the quantity, instead of adding to the fusibility of the slag, has a precisely opposite effect. Such, at least, is apparently the case in smelting the ironstone of Cleveland, judging from the slag formed upon one occasion when, by way of experiment, all limestone was withdrawn from the charges. The slag was well fused, but the iron

became hard, and contained above three times the usual content of sulphur.

The darkened appearance of the hearth, spoken of by Dr. Percy,* is susceptible of another explanation than that of an actual general refrigeration of this region. It is more probable, it occurs to me, that the cold air meeting the slag and iron chills a small portion of the fused matter as it passes the tuyeres, but this, of course, is not the action of air on carbon, but of air upon slag and metal. When, on the other hand, the melted contents of the furnace trickle down before a current of heated air, they also, no doubt, are chilled, but not to the extent to deprive them of fluidity before they pass beyond its influence, and, in this way, there is no accumulation of solidified matter, which gives rise to the prolonged tube or "nose," as it is termed, reaching far into the hearth.

To account for this supposed increase of intensity in the heat of a hot-blast furnace, Dr. Percy quotes the experiment of the Swedish metallurgist, Mr. Sandberg, who observed that heated oxygen combines more rapidly with incandescent carbon than cold oxygen, and that in consequence there "must be a proportionate increase of temperature, for *cæteris paribus* temperature will be in the direct ratio of rapidity of combustion."

Ordinary combustion of carbon is generally spoken of as an oxidizing of the carbon about to be burnt, and this no doubt, looking at the office played by oxygen in combustion generally, is a convenient mode of expressing the action. But as combustion of carbon is no more the oxidation of this element than it is the carburizing of oxygen, it will be more convenient, for our purpose, to speak of it in this inverted manner. Now, when oxygen is propelled into *a blast furnace*, it becomes rapidly carburized to its utmost limit of saturation, *i.e.*, it is speedily converted into CO. This union with carbon is so instantaneous that free O is never mentioned as the constituent of any analyses of furnace gases I have met with or made. Hence if there was any difference in the extent to which the oxygen became carburized as between cold and hot blast, it would manifest itself in the larger quantity of CO_2, where the rapidity of combustion was the least, because in this case the oxygen is unable to take

* "Metallurgy of Iron and Steel," p. 427.

up as much C as when the union is more speedy, and this slowness of combustion is what Dr. Percy concludes will happen when the oxygen is driven into the furnace as cold blast.

Were it consistent with observation that this carburization of oxygen were retarded by the want of heat in the oxygen, I would submit that the very opposite effect to that mentioned by this writer would ensue at the tuyeres, *i.e.*, instead of a cold blast furnace having a lower temperature generated in the hearth, it would be much hotter, inasmuch as the heat evolved by carburizing O to the lower state of CO_2 is three times that produced by the more perfect carburizing of the blast, which happens when CO is the product.

We need only refer to what has been said in Section XXX. on the origin of the heat in the blast furnace to be satisfied that no temperature to which it would be possible to raise the air could compensate for such a difference as exists between carburizing O to the condition of CO_2 and CO, 8,000 calories being the product of one unit of carbon passing to CO_2 against 2,400 when the other oxide is produced.

The following analyses, given in Dr. Percy's work, show the volumes of CO and CO_2 per 100 volumes of the gases:—

Furnace.	Blast.	Gases collected at	CO.	CO_2
Clerval—	cold	Tymp ...	39·86	... ·93
Do.	190°C. (374°F.)...	18in. above tuyeres	41·59	... ·31
Eisenerz,	200°C. (392°F.)	Level of tuyeres	22·06	... 11·60

Is there, however, any valid ground for asserting that the carburizing of the injected oxygen is slower when it is cold than when hot? In the analysis, referred to by Dr. Percy himself, of the gas taken from the tymp (about the level of the tuyeres) of the Clerval furnace blown with cold air, there are 39·86 vols. CO to ·93 vols. CO_2. At the same place, when the blast was used at 190°C. (374°F.), a specimen of gas 18 inches above the tuyere, and therefore vertically about as far from the point of entrance of the O as the other was horizontally, 41·59 vols. of CO were accompanied by ·31 vols. of CO_2. This difference, small as it is, must be regarded rather as accidental than general, and, under no circumstances, can account for any great change in the actual temperature.

The information, however, elicited by an analysis of the Wear gases, taken from the level of the tuyeres, shows that carburization

of the oxygen is not more rapid with the blast at 460°C. (860°F.) than it was at Clerval with cold air.

	CO.	CO_2
Exp. 744.	37·5	·76
„ 745.	37·7	·76
„ 746.	35·8	2·10
„ 747.	31·7	1·1
„ 748.	33·8	·8

All this argument, nevertheless, would have to give way to the fact, could it be established, that the temperature of the hearth of a hot-blast furnace really did exceed that of one blown with cold air.

I have already (Section XXXVI.) alluded to the difficulty experienced in obtaining, by means of the calorimeter, any data sufficiently uniform to enable me to determine the temperature of the contents of the hearth of a furnace. In the same place, however, I have given my reasons for believing that the cause of the difference between white iron and grey was simply one of temperature. This was done, it may be recollected, by heating white iron to a point known to be sufficient to produce grey iron, and the change was effected, *i.e.*, the white became converted to grey. The plan followed consisted in plunging a bar of white iron in a current of slag as it issued from a furnace producing iron grey in quality.

Since writing the account of this experiment I have, by the kind assistance of my friends, the Messrs. Kitson, of the Monkbridge Works, at Leeds, satisfied myself of its correctness by another mode of procedure.

Exp. 749. About 60 lbs. of Clarence white pig iron was melted in one of their Siemens steel melting furnaces, and run into a mould of green sand forming a cube of 6 inches on a side. With the exception of a trace of white at one corner, the whole was converted into uniform good grey forge.

Exp. 750. The same quantity of the same iron as that used in the previous experiment was melted on a Saturday, and allowed to remain over the Sunday in the furnace, during which time it cooled slowly. The block, having a maximum diameter of 6 or 7 inches, was entirely grey, chiefly No. 3, interspersed with some No. 4.

It seems, therefore, not unreasonable to accept the iron made in any particular furnace as a species of pyrometer for determining, if not the actual temperature of its interior, at all events of establishing a comparative test between it and that of another.

If then, temperature is the governing cause of quality of iron (numbers), it is highly improbable that the same degree of heat intensity is *cæteris paribus* making white iron in one furnace and grey iron in another. It does seem more rational to suppose that if two furnaces are both running, say No. 3 iron, from the same materials, one blown with hot air and the other with cold, they are making the same quality, because the temperature is the same in both.

This admission as to parity of temperature, of course, does not presuppose that the heat evolved by the combustion of carbon with hot air is not more intense than that arising from cold air; but what I affirm is that, in consequence of the greater amount of iron and slag being melted with a given weight of fuel, when burnt with hot blast, the actual temperature in the crucible of such a furnace is probably lowered to that of one blown with cold air having a smaller weight of material to fuse.

In recent years, by raising the temperature of the blast to 485°C., the consumption of coke has been reduced to 28 cwts. per ton of iron when smelting Cleveland ironstone in a furnace 48 feet high, and in which probably more than 60 cwts. (the quantity named in connection with the Scotch furnaces) would at least be required with cold air. Of the carbon in the 28 cwts. of coke mentioned above, after deducting that dissolved by the CO_2 of the flux, about 25 cwts. would be burnt to CO at the tuyeres.

25 cwts. C × 2,400	...	=	60,000 calories.
Blast will contain about	...	...	16,000 „
			76,000 „

The intensity, however, of this quantity of heat has been shown in Section XXXVII. to be greatly augmented by that intercepted by the materials and brought down again to the zone of fusion. This was in one case proved to amount to 70 per cent. of that actually evolved by the quantity of fuel consumed to produce one ton of iron. So far as intensity therefore is concerned, we have to deal with

Units from coke per ton of iron ...	... 76,000	calories
Plus 70 % intercepted and brought back	... 53,200	„
	129,200	„

In like manner, with a consumption of 60 cwts. of coke, about 54 cwts. of carbon would be burnt at the tuyeres to CO.

54 cwts. C × 2,400 ...	= 129,600	calories
Plus heat in blast, about	2,400	„
	132,000	„
To which if we add for intercepted heat 70 per cent.	92,400	„
There is obtained	223,400	„

Now, it seems on the face of it, incredible that the mere addition of 16,000 cwt. heat units, in the place of 2,400, should so alter the intensity of heat in the crucible as to make all the difference in the work performed.

Upon a former occasion* I called attention to the fact that whereas in the hearth of a blast furnace the C was burnt to CO, in the hot-air stoves it left the fireplace as CO_2. This of itself would enable each unit of carbon to give 3·33 times as much heat when burnt in the hot-air apparatus as when burnt in a blast furnace. The advantage, however, resulting from this change in the manner of combustion, would be considerably diminished by the great loss from radiation, and at the chimney of the heating stove. This is conclusively exhibited by the fact that whereas at least 4 cwts. of coal, equal to 32,000 cwt. heat units, are used per ton of iron in the stoves of a 48-feet furnace, only 16,000 find their way through the tuyeres.

Upon the same occasion I alluded to the circumstance that the mere alteration of the proportion of ironstone to coke conferred an advantage upon the hot-blast furnace by presenting to the ascending gases a greater quantity of matter having a higher heat-absorbing power, ironstone being superior in this respect to coke.

Exp. 751. To determine the relative powers of coke, limestone, and ironstone, a cast-iron cylinder was provided, four feet long and one foot in diameter, closed at each end. The material

* "Chemistry of the Blast Furnace. Transactions Chem. Soc. of London, 1869."

to be operated on, broken as nearly as possible to the same size, was introduced into the cylinder, which it filled, and by means of an inch pipe hot air was introduced at the low end and allowed to escape at the upper. This was continued until a thermometer inserted at the top became stationary.

Numbers of a very constant character were obtained when using the same substance, and from these were deduced that bulk for bulk, taking coke as unity, the intercepting power of

Coke being	... ...	1·00
Cleveland calcined ironstone was	...	2·00
Limestone	„ ...	1·60

These figures, however, indicate that the heat-absorbing power of a hot-blast burden is only about 10 per cent. superior to that of cold blast.

Under these circumstances, therefore, it is clear that neither modifications of the circumstances just mentioned can account for more than a very small proportion of the actual saving effected by the use of heated air.

In the treatise by M. Dufrenoy, pointed allusion is made to a fact in connection with the use of hot air in France when using certain ores, from which it would appear that practically no saving whatever resulted from its application to the smelting of the mineral used at La Guerche,* which, although containing only 42 per cent. of iron, gave a ton with 25 cwts. of fuel and cold air.

Mons. Dufrenoy dismisses, what seems to me a very important matter in connection with the theory of the hot blast, with the simple observation that the figures, in connection with the Guerche furnace he quotes, are "not favourable to the use of hot air," and I am not aware of their having attracted the notice of any subsequent writer on this interesting question.

It may be remarked that the "extraordinary saving" mentioned by most authorities as consequent upon the use of the hot blast seems to have been regarded in the light of one of general application. At all events, little stress has been paid to the well-known

* This furnace was compared, by Dufrenoy, with a neighbouring one at Torteron, using the same kind of fuel and ore, to which heated air was applied. The only change caused by the altered mode of working was, that the iron, instead of being white, as it was when cold air was used, became grey.

fact, that in many instances the economy of fuel was much less than in Scotland, where its much greater importance has, so far as I know, formed the usual ground upon which its powers were considered.

Dufrenoy himself, for example, mentions the circumstance that at the Plymouth Iron Works, near Merthyr Tydvil, a ton of iron was produced with 53 cwts. of raw coal, and that by the use of hot air it could be reduced to 36 cwts. The saving, 17 cwts. of Plymouth coal, only represents 13 cwts. of coke, instead of the 22 given as that effected in Scotland by hot air.

Now, the problem I would suggest to those who allege that "calorific intensity in what may be considered the most active part of the furnace is higher in the case of hot blast than in the case of cold blast" is, whence arises it that the addition to this assumed intensity of heat in the crucible is attended with such different results as those just mentioned ?

I cannot help thinking that the answer to the above enquiry is to be sought for in an entirely different direction, and, in pursuit of which, may be quoted the results of certain experiments described in the earlier sections of this work. In these it was conclusively proved that differently prepared specimens of oxide of iron and different kinds of ore, all being peroxides, were very differently affected by the application of heated CO. Thus, in about seven hours, at a temperature of 410°C. (770°F.), in

Exp. 30.	Fe_2O_3 from calcined nitrate, lost	72·7	%	of its original O.
„ 29.	„ precipitated	66·7	„	„
„ 28.	„ from calcined $FeSO_4$	61·7	„	„
„ 35.	Lancashire hæmatite	57·4	„	„
„ 34.	Calcined spathose ore	28·4	„	„
„ 33.	„ Cleveland ore	20·7	„	„
„ 26.	„ „	9·4	„	„

Now, the two experiments 33 and 34 may be taken almost as an exact type of what happens in the Plymouth and Scotch furnaces respectively. We have calcined spathose ore losing its oxygen with nearly one-half more rapidity than that of the Cleveland hills. This would mean that for the purpose of complete reduction we should have to expose the last-mentioned mineral for a one-half longer period of time than the other.

Let us see how this difference in susceptibility to reduction

accounts for the greater consumption of fuel in the case of the black band, as compared with the ore smelted at the Plymouth Works, both of which will be regarded as yielding the same per centage of iron.

In the first place, it is obvious that it cannot be from any difference in the cooling effect of expanding air, as the blast is cold in both cases; neither can it be rapidity of combustion causing intensity of heat, because, if both furnaces burnt the same quantity of fuel in a given time, the Scotch ore would still continue to require the larger quantity of combustible per ton of iron.

It can hardly be alleged that the same quantity of iron and slag to be melted derived from black band can require for their fusion in the hearth one-half more heat than do the same substances from the mineral operated upon in South Wales.

Instead of all this, let us suppose that in the hearth of a blast furnace a certain mixture of reduced iron and earthy matter had to be fused, with the minimum quantity of fuel capable of evolving, with cold air, the necessary heat. From the combustion is generated a certain quantity of CO, which we will further suppose to be able to carry off all the oxygen contained in the minerals without difficulty. This carbonic oxide now commences to flow through the oxide of iron at a rate determined by the rapidity of the combustion and fusion at the tuyeres.

Reduction is effected by the current of CO, and in the case of the Plymouth mineral it takes place at such a rate that by the time about 40 cwts. of coked fuel, the produce of 53 cwts. of Welsh coal, are burnt at the tuyeres, deoxidation has been completed, and carbon-impregnated iron is ready for fusion.

If, however, another ore, say black band, parts with its oxygen much more slowly than that just described, it is certain that the exposure to the reducing agent must, by so much, be prolonged. This, however, cannot be accomplished if the rate of fusion continues the same as it was in the Welsh furnace. There is, therefore, no alternative, in a small furnace, but to retard fusion by the addition of fuel. This reduces the weight of material to be melted, and at the same time supplies an *extra* quantity of CO, which also assists in overcoming the want of susceptibility of reduction inherent in the more refractory ore.

The law, therefore, which I believe determines the whole ques-

tion of differences of fuel required to smelt ores of different kinds, but containing the same percentage of metal, and which constitutes the value of the hot blast is—*that the rate of reduction must not proceed less rapidly than that of fusion.*

It must not be imagined that if a sample of the Scotch black band and one from Plymouth were exposed to a current of heated CO that deoxidation would necessarily take place exactly at the rates indicated by the quantity of coke required respectively to smelt them—at the same time a fair idea would in all probability be obtained by the information afforded by such a trial.

In the hearth of the Scotch furnace there will be evolved for each ton of iron something like 132,000 cwts. heat units, against 88,000 at Plymouth, both being blown with cold air. It will be observed that in both cases the actual quantity of heat is greatly in excess of what can be possibly required for fusion of iron and slag. This excess, after satisfying the requirements of the crucible, is carried off in the gases, a much larger quantity, of course, in that where the consumption of fuel per ton of iron is the largest. The application of the law just laid down to the two examples now considered consists in supposing that under the circumstances of size of furnace, &c., whereas 60 cwts. of coke was needed in Scotland to bring the reducing and fusing powers in harmony with each other, the coke from 53 cwts. of raw coal (about 40 cwts.) sufficed to effect the same object at Plymouth.

It may not be altogether out of place, before proceeding further with the present argument, to examine a little in detail the performance of the Guerche furnace, which, although of very small dimensions, when using ore of about the same richness as that of Cleveland, and requiring the same quantity of limestone, produced with cold air a ton of metal for 24·92 cwts. of fuel.

This of course means that, notwithstanding the small capacity, the ore employed surrendered its oxygen so freely that the current of gases proceeding from the above-named quantity of fuel became saturated with oxygen by the time they reached the throat, and quite as rapidly as the carbon burnt at the tuyeres could fuse the reduced metal and slag.

No account is handed down to us of the composition of these gases; indeed, at the period of M. Dufrenoy's observations, this subject had received but small attention. All we can, therefore,

do is to consider how far the quantity of fuel consumed can be made to correspond with the actual amount of heat required.

The fuel employed consisted of two-thirds charcoal and one-third coke, but as the work done at Guerche was compared with that of another furnace (Torteron), also using the same mixture of combustible, but blown with hot air, and as we are now considering the quantity of heat, which is the same practically from coke and charcoal, the presence of the latter may be disregarded.

Fuel consumed per ton of iron ...		24·92 cwts.	
Ore		48·74	
Limestone		11·16	
Estimate of heat development—			
Fuel burnt...	24·92		
Deduct, say 10% for impurity	2·49		
		22·43	
C in limestone carrying off equal weight from fuel ($CO_2+C=2\,CO$) ...		1·32	
			units.
C burnt to CO		21·11 × 2,400	= 50,664
C of this CO burnt to CO_2, say ...		6·00 × 5,600	= 33,600
Heat units in blast from compression, say			2,000
			96,264

Heat absorption as per table in Section XXVIII. :—

Evaporation of H_2O in fuel	312	
Reduction of Fe and carbon impregnation...	34,548	
Expulsion of CO_2 from limestone 11·16 × 370...	4,129	
Decomposition of this CO_2 ... 1·32 × 3,200...	4,224	
Do. H_2O in blast	2,720	
P, S, and Si reduced, assumed one-half* ...	2,087	
Fusion of iron and slag	23,100	
Transmission of heat through sides	3,658	
Tuyere water	nil.	
	74,778	
Leaving (which is more than ample for escaping gases)†	11,486	
		96,264

* Probably less P and Si than in Cleveland iron.

† In all probability, 6 of C, burnt to CO_2, is 1 cwt. in excess of actual quantity, which would reduce heat in gases to 5,886 units.

Thus it will be observed that even with cold air, under favourable conditions, a ton of iron can be obtained from an ore of only medium richness with 25 cwts. of fuel.

Suppose now in this Guerche furnace, containing, probably, only 3,000 to 4,000 cubic feet, it were attempted to smelt Cleveland ore, which, so far as yield of iron and consumption of flux are concerned, nearly approaches that affording the results just given.

In order to prolong the contact between the ore of Yorkshire and the reducing gases, as well as to increase the deoxidizing power of the latter, probably not far short of 65 cwts. of fuel would be necessary to obtain a ton of iron. No less than 40 cwts. being thus expended in establishing the proper relations between the co-efficient of fusion and that of reduction.

There is, however, another method in making amends for this want of harmony between the two functions of the blast furnace. Instead of delaying the fusion of solids, and increasing the energy of the reducing gases by the addition of CO, the same object may be attained if contact is prolonged in a furnace of larger capacity.

In illustration of this mode of action, I will again quote from the experience and figures kindly communicated to me by my friend, Mr. Horton, of the Lilleshall Iron Company.

In furnaces having a height of 53 feet, driven with cold air, an ore poorer than the Scotch black band, and containing about 43 per cent. of iron, calcined, was smelted with about 40 cwts. of coke, affording another case of an ironstone more reducible than those which hitherto have formed the favourite basis of estimating the effects of the hot blast.

Here the available heat may be taken at fully 25,000 cwt. units beyond that which could possibly be absorbed in the process, and which, in consequence, must have escaped from the throat.

Mr. Horton, encouraged by the example of the Cleveland ironmasters, proceeded to add to the capacity of his furnaces. Having to deal with materials entirely different in character from those used in the neighbourhood of Middlesbrough, this gentleman deemed it prudent to proceed with caution, and therefore contented himself with raising his furnaces to a height of 71 feet.

The result was most satisfactory, and at Lilleshall may be seen six cold blast furnaces, making good foundry iron with 27 to 28

cwts. of coke, which is fully as small a quantity as would have been required in the old furnaces of 53 feet, had they been blown with an air at 450°C. (842°F.)

Possibly, looking at the tender nature of the coke at Lilleshall, and the size of the ironstone, Mr. Horton may have been quite right in not venturing on the adoption of the dimensions found now so commonly on the banks of the Tees, where the coke is dense and the ore in large pieces. Were it possible, however, to treat the Shropshire minerals in a furnace 80 or 85 feet high, so far as fusion and reduction are concerned, I apprehend there is little doubt the coke consumption might be reduced to that of Guerche, viz., 25 cwts. to the ton of iron, for it is obvious with an escape of 25,000 cwt. units there is still a considerable margin for economizing.

Had such an alteration, as that just described as having been made at Lilleshall, been carried into effect before the introduction of the hot blast, even in the then state of knowledge of the theory of iron smelting, the inference would have been inevitable, that the advantage obtained by raising the furnace was solely due to its imperfect nature—in short, that just as the Stückofen was inferior to the first high blast furnace, so was the furnace of 53 feet at Lilleshall inferior to that of 71 feet.

Like the discovery of Abraham Darby in using mineral fuel for iron smelting, it is impossible to overrate the value of the hot blast at the period of its first introduction. Indeed, I am not prepared to say that for the black band of Scotland, it may not have nearly as great a value still, due to some mechanical difficulties in its treatment, such as forcing the blast through a very high column composed of this mineral and raw coal, and which, therefore, may render a lower furnace necessary, unless when assisted by Mr. Ferrie's coking chambers. In this opinion I am guided by the alleged want of success experienced by the Scotch ironmasters, when they raised their furnaces in former years, and by the opposite results obtained by Mr. Ferrie.

Apart from any such impediments as those just mentioned, what I consider as beyond all doubt is, that the value of the hot blast at the period of its invention was, so far as any "extraordinary effect" is concerned, solely due to the defective nature of the furnaces then in use, and that when this is remedied, 1,000 units

of heat in the blast can be as easily accounted for as a similar quantity derived from the combustion of fuel in the hearth.

We have only to appeal to the knowledge afforded at Lilleshall in verification of this statement. Foundry iron is there produced with cold air by, say, 27½ cwts. of coke. Let 12,000 heat units be thrown in with the blast, which are equivalent to 4 cwts. of coke burnt with air at 485°C. to CO. This at once is a reduction of the fuel consumed to 23½ cwts., which is probably not far off the actual quantity a furnace of 71 feet would require.

Speaking from the accumulated knowledge respecting the action of iron smelting obtained in recent years, we have seen that valuable as the hot blast was when applied to furnaces of moderate height, it was far from remedying entirely the structural defect alluded to above, for it was not until those of the largest description had their capacity doubled that something like the full economy in smelting the ore of Cleveland was reached.

Returning for a moment to the enlarged Lilleshall furnaces, we have seen that precisely the same object was secured whether, as in their case, an addition to the size was the means employed, or the blast was heated. Exactly the same law holds good with the furnaces of the former moderate dimensions heated with air at 450°C. They may be enlarged, as has been done in most cases in the North of England, or they may be retained of lesser dimensions, and fed with air at 600° to 700°, according to the mode pursued at Consett.

The limit, or what I have already stated, and what, in a future section, I shall again state, I consider to be—the limit of economy—once reached, very large capacity and very highly heated blast simply tend to neutralize each other.

It may be urged that whether a certain number of heat units is communicated to the blast, and, rising upwards, is intercepted and returned downwards, or whether the same result is brought about by an increase of capacity in the furnace, the effect upon the temperature of the crucible will be the same, and that in each case, it may be supposed, the heat of the latter will be augmented.

Not having access to any furnace (close topped) using cold blast as would permit an accurate examination of the actual temperature of the escaping gases, after an addition to its capacity has been made, I have been unable to prove, by actual experiment, what the

effect has been of such increase of size, and of comparing such results with those at furnaces of similar dimensions using hot air, both being engaged in smelting the same kind of ironstone. Under these circumstances, I have been compelled to make use of such data as I possess, which, unfortunately, are not the best fitted for the object in question, because the materials under treatment differed considerably in their nature.

The furnaces selected for the purpose were two at Cyfarthfa, 52 ft. high, one blown with cold air, and the other with its blast at 332°C. (610°F.) The latter, using fully 8 cwts. less fuel per ton of iron than the other, nevertheless, had its gases passing off 60°C. (108°F.) hotter than those of the cold blown furnace.

It was mentioned, in the present section, that waste of fuel in the blast furnace arose from a want of harmony between the operations of fusion and reduction, the latter not keeping pace with the former. I have shown how this was remedied by increasing the opportunity the reducing gases had for acting on the oxide of iron. This was effected by a prolongation of contact, obtained by enlarging the furnaces, but we have only to refer to those experiments which were undertaken for the purpose of ascertaining the laws which regulate the conduct of the substances met with in the process of smelting an ore of iron, to see that the shorter period of contact can be maintained, or even curtailed, provided the energy of the reducing agent is augmented. Thus in Exp. 36, while calcined Cleveland stone lost 37·3 per cent. of its oxygen in eight hours, by being exposed to CO at a temperature of 410°C. (770°F.), the same ore lost (Exp. 49) 63 per cent. at a dull red heat in the same time, and 90 per cent. (Exp. 50) was expelled in $3\frac{3}{4}$ hours, the temperature being that of bright redness.

I infer, therefore, that the improvement by the use of the hot blast, is not due to any additional heat reconveyed to the hearth, but that such heat is utilized in promoting the energy of the reducing gases in the upper zone, and having done this, it is carried off from the outlet of the furnace. The reasons have been mentioned to show it is unlikely that the temperature of the hearth is really sensibly increased, and also that a very small addition to that of the escaping gases greatly augments the power they possess of causing reduction. It seems to me, therefore, much more probable that the advantage derived from the use of

heated air must be ascribed to the increased temperature in the upper region of the furnace, by which the process of reduction is hastened in a corresponding ratio. In this way, although fusion goes on at an increased speed in the hearth of hot-blast furnaces, on account of the decreased quantity of fuel by which it is effected, as reduction experiences a still greater acceleration, the two operations are carried on in harmony, in point of time, with each other.

If then, we take the case of a cold blast furnace of 52 feet, consuming any given quantity of coke per ton of its product, I say that the temperature of the hearth is the same as that of any hot blast furnace producing the same quality of metal, from the same materials, and that the action of reduction being too languid in comparison with the process of fusion, a loss of fuel is the result, in the manner already described, and that this loss may be remedied either by prolonging contact, or by increasing the energy of the reducing gases by communicating heat to the air used for effecting the combustion of the carbon in the hearth. Further, I say that when no such want of harmony between the two branches of the process obtains, as in the case of the furnace at Guerche, no such stimulus as that afforded by the hot blast is required. From this latter statement it must not be concluded that no saving in fuel would accrue to a furnace using 25 cwts. of coke to the ton of iron by the addition of a high temperature to the blast. The calories, however, so contributed would be found to correspond, in all probability, very closely with those afforded by so much coke economized by the change.

I may be excused, if I parenthetically observe the great advantage to be derived from a perfect understanding of the fundamental principles which lie beneath a process so essentially chemical as that carried on in an iron furnace. It seems scarcely possible to imagine that had the ironmaster, before Neilson's time, been aware, and, being aware, had seriously considered, that in many cases, out of 133,000 calories actually evolved, he only beneficially applied 49,000, or about one-third of the whole, we should not have had to wait for the accidental observation of a thoughtful gas works manager, before attempting to avoid part of the loss of 63 per cent. of his fuel, which might have been done by the simpler plan of increasing the size of the furnace, in which, if the remedy be not

perfect, it is at least as much so as that effected by the hot blast itself.

Greatly curtailed in point of importance, as I deem the use of hot air to be, since the adoption of recent improvements, I would not have it supposed that it has to be regarded in any other light than that of a very powerful and valuable aid to the iron smelter. Its mode of application is so direct and simple that heat may be conveyed in greater or less quantity, as may be required, at once to the focus of most intense temperature, without waiting for a change in the materials which requires some time before it reaches the tuyeres. This assistance too is afforded by a fuel, the escaping gases, which in many cases, if not so applied, would be wasted. These attributes, even in their modified form of usefulness will, in my opinion, ensure for Neilson's discovery a lasting position in the science of iron metallurgy, and will preserve for his name an exalted place among the most illustrious of those who, by their ingenuity, have advanced the industrial resources, and, therefore, the national importance of their country.

SECTION XL.—ON THE EFFECT OF THE HOT BLAST ON THE QUALITY OF THE IRON.

Like many new inventions, the hot blast met with considerable opposition at the period of its introduction. In Scotland, including the coal used at the blowing engine, the waste incurred in coking the coal, and all other items, the reduction in the quantity of fuel often amounted to 75 %. According to M. Dufrenoy, the money value arising from this source, and that derived from a diminution in the general working charges, from the increased make, amounted to £1 5s. 11d. per ton of iron, made with air heated to 322°C. (611°F.)

With the Scotch pig iron makers, this difference in cost bore down all resistance, and every establishment in that part of the kingdom

was speedily blown with hot blast. Wales, up to the period of Neilson's discovery, was, according to Dufrenoy, able to produce pig iron at a lower rate than any other locality in Great Britain. Unfortunately for the Principality, the mere act of heating the air completely changed the aspect of affairs, for while this modification of the manufacture was followed by a saving of 26s. per ton in Scotland, something like 1s. 8d. was all the benefit its adoption was, according to the French engineer, able to afford to the Welsh ironmaster.

The Glasgow makers enjoyed immense advantages in the possession of their cheap and rich ironstone, but, unfortunately, these were, in a great measure, neutralized by its refractory nature when smelted in small furnaces (50 feet) with cold air, a difficulty which involved the consumption of a large quantity of fuel, raised at a higher price than that of the Welsh coalfield. This objection was remedied by the addition of 600°F. to the blast.

In Wales, on the other hand, the ironstone was poor, but easily smelted; the coal was cheap (3s. 7d. per ton, Dufrenoy states), rich in carbon, so that 50 to 54 cwts. were able to produce a ton of metal. This quantity could only, it was estimated, be reduced 17 cwts. by the use of the hot blast, from which had to be deducted 6 cwts. consumed in the heating apparatus, leaving a net gain of 11 cwts., equal to the saving of 1s. 8d. per ton, of which 1s. had to fall to the share of the patentee.

After some unsuccessful litigation in disputing the legal position of Mr. Neilson, many of the Welsh ironmasters discontinued the practice of heating the blast, it being pretended that the trifling saving in cost was more than swallowed up by the inferior quality of the iron made by its means.

However sincere these manufacturers may have been at the time in question, further experience has modified their ideas, for at the present day by far the larger number of furnaces in Wales is blown with hot air.

It is now upwards of forty years since Neilson patented his discovery, and it is not a little remarkable that this question of quality cannot be considered as entirely settled yet. If the matter had to be judged by the acts of the majority of the manufacturers, then undoubtedly it might be inferred that the present cases, so few are they, where cold blast is still adhered to, might be regarded

as the last signs of life in a struggle against speedy extinction. Large, however, as this preponderance of opinion may be in favour of hot air, it has the objection, it may be urged, of being entertained by those who may be supposed to prefer its use on account of the cheapness it has been the means of introducing into their process, and the great command it gives over the operation.

With every wish to deal fairly with the disputed point of quality, its decision is surrounded with much difficulty, and is one which requires great experience, before any individual is justified in speaking with the necessary confidence even on facts capable of more speedy demonstration than those appertaining more immediately to the use and durability of the product. In illustration of this, I may observe, on referring to some early note-books of visits to the Welsh works, that the opinion was then pretty generally entertained that the whole of the advantages obtained in the blast furnace by the use of hot air was, by the waste of iron and defective quality, lost in the forge and mill.

The present generation, however, as a rule, has turned its back on the creed of its predecessor, and the advantages of hot blast, at all events as a matter of economy, is, in our time, universally admitted. As regards the alleged loss in the process of converting the pig into malleable iron, I have the indisputable authority of my friend, Mr. Menelaus, of the Dowlais Works, for stating that this is a mere illusion, and that small, comparatively speaking, as the saving of fuel in the blast furnace is in Wales (about 15 cwts.), the advantages of hot air cannot be denied by any one who has paid proper attention to the subject. This it must be recollected, is, of course, not a carelessly adopted view, but one which is the result of comparing whole years' operations conducted under the two systems.

During the recent visit of the Iron and Steel Institute to Staffordshire, I made the subject a matter of constant enquiry. I cannot say the answers received were universally in one direction, but there is no manner of doubt the large preponderance of opinion, and this from makers of immense experience, is, that from the same materials there is no appreciable difference between hot and cold blast pig nor in the malleable iron afforded by the two kinds of metal.

My experience in foreign countries leads me to believe that this is the view entertained by the great majority of those producers of

the fine descriptions of charcoal iron, whose position in the market is entirely dependent on the world-wide reputation of their limited make. With few exceptions, I found these Continental manufacturers had applied hot air to their furnaces; as, for example, in Norway and Sweden, when treating the pure magnetic oxides of these countries, in Styria and Carinthia, for smelting the fine spathose ore of Eisenerz and Lölling, and at Fullonica, when using the specular ore from the neighbouring island of Elba.

At Dannemora, it is true, they adhere to cold air, on the ground, as I was informed, that the quality of their well-known brand had suffered by an attempt to use hot air.

Professor Tunner* on the other hand, who has had large experience with the manufacture of the pure charcoal iron at Eisenerz, asserts positively that deterioration is no necessary consequence of the use of hot blast..

When such very minute quantities of certain substances, such as P, S, Si, &c., are known to be capable of affecting in an unmistakeable manner the properties of iron in which they occur, it is, perhaps, an act of over refinement to reason upon their being present in greater or less amount from our presumed acquaintance with the nature of the smelting process, when carried on by means of air heated or otherwise.

It may be urged, and perhaps reasonably so, that our knowledge of this subject is too limited to deal satisfactorily with so delicate a matter as that in question; at the same time, we must make the best use we can of the information we possess, and the argument based thereon must be judged accordingly.

Viewing the action of the blast furnace comprehensively, I have regarded the actual work done as performed identically in the same manner, whether the air is used hot or cold. Thus, in the Lilleshall 71 feet furnaces, we have the combustion of about 28 cwts. of coke affording the necessary heat for smelting iron from an ironstone yielding 40 to 43 %, by giving the gases time enough to become saturated with O, and so to communicate their sensible heat to the descending materials, that when the latter reached the tuyeres the store of heat they contained, added to that evolved by the combustion of the fuel, sufficed for the required duty, without any heat

* Russland's Montan Industrie insbesondere dessen Eisenwesen. Leipsig, 1871.

being communicated to the blast. If the furnace, instead of having a height of 71 feet, had only 48, the work was inefficiently performed, and had either to be supplemented by the hot blast or by the consumption of a larger quantity of fuel in the manner already explained. By an increase of capacity and the use of hot air, a further economy of fuel may be effected, and this continues until the gases are fully saturated with oxygen.

In effect, then, as has been already stated, for a similar quality of iron, an identity of temperature ought to be found in every furnace, whether the air which enters it is hot or cold. If this be so, then in the matter of temperature there is no reason why iron made in either way should differ materially.

If, on the other hand, as has been and is often alleged, the effect of heated air is to detoriorate the quality of the pig iron, we might reasonably expect that this deterioration would keep some kind of pace with the elevation of temperature conferred on the blast.

In comparing hot with cold blast iron, I speak with hesitation, from my want of experience with the latter, but in dealing with iron made in furnaces blown with air at about 350°C. (662°F.) up to 500°C. (932°F.), I labour under no such disadvantage. I may, therefore, confidently state, from my own personal acquaintance with both, that the quality of the product has in no way suffered by the change from the lower to the higher of these temperatures of blast. Indeed, I may go further, and give it as my own opinion that there has been an actual improvement, which I attribute to the use of a less quantity of fuel, for, if reference is made to Section XXXV., on the behaviour of P and S in the blast furnace, it will be seen there is an appreciable quantity of both these elements in the coke. Anything, therefore, which lessens the extent to which these acknowledged hurtful ingredients enter the furnace must be beneficial, and one cannot be surprised that the iron has not suffered by raising the temperature of the blast, accompanied, as this has been, by a diminution in the quantity of fuel.

Looking back at the figures contained in the section mentioned above, it will be seen that the phosphorus entering the furnace, when using hot air, for each 100 parts of iron produced, amounted to 1·578, and the sulphur to 4·456. Were this furnace using 3 tons of coke per ton of iron, the phosphorus would be raised to 2·055, and the sulphur to 7·3 parts per 100 of pig.

These arguments, based on the action of the blast furnace, so far as they go, would point to the conclusion that hot blast, far from acting hurtfully on the iron smelted by its aid, will produce a marked improvement by the change in its temperature. At the same time, however, we must not overlook the fact that in the hearth of the blast furnace there is constantly occurring a series of very complicated and, perhaps, not very well understood, chemical changes, which have been touched upon when speaking in Sections XXVI. and XXXIV. on the generation and decomposition of certain cyanogen salts. Whether or not slight changes in local temperature may affect the order of chemical action, which appears very active near the tuyeres, it is impossible, in our present state of knowledge, to say.

The experience in the manufacture of Bessemer steel affords some information to guide us in the consideration of this intricate problem now under consideration. If a sample of pig is delivered to the bar iron maker, containing a large percentage of phosphorus, the action of the puddling furnace removes by far the greater proportion of this substance.

Exp. 752. A specimen of pig iron was ascertained to have associated with it P 1·33 per cent.
S ·158 „
the puddled iron made from it contained, of P, ·29 per cent.; and of S, a mere trace.

Exp. 753. A second sample of pig iron, containing about 1½ per cent. of P, yielded a puddled bar, giving only ·33 per cent. of this substance.

In the Bessemer converter, no such removal of phosphorus takes place, and as its presence in quantity amounting to less than one-tenth per cent. is fatal, the steel maker has no alternative but to employ pig iron almost entirely free from this element. Sulphur, too, is equally shunned by the producer of Bessemer steel. Now, if the action of hot air, in the blast furnace, tended in any way to concentrate the quantity of either phosphorus or sulphur in pig iron, it is clear its use would be more carefully avoided in the manufacture of that intended for the steel works than that destined for the manufacture of bar iron, inasmuch as the puddling process is capable of removing partially, at all events, the phosphorus, which is not the case with the Bessemer converter. This view of

the question, of course, confines the cause of deterioration to sulphur and phosphorus. It is possible that some other ingredients may, by their presence, prejudicially affect the quality of iron, such, for example, as silicon, but I am not aware that those who advocate the use of cold blast have ever succeeded in demonstrating that the superiority of iron, so smelted, was indebted for its alleged higher excellence to the absence of any particular ingredient or ingredients found in metal produced with hot air.

At the present time, when the relative merits of the two systems of manufacture are compared, reference is very generally made to the high character of certain well-known brands of iron, which being produced exclusively by means of cold blast are regarded as affording incontrovertible proof of the superiority possessed by the ancient mode of smelting.

It is almost superfluous to say that it is in the highest degree unphilosophical to institute any comparison between hot and cold blast iron, unless in each case the minerals are precisely the same. To some extent this has been done, and it would appear that, according to the experiments of Fairbairn and Hodgkinson, already referred to, when the hot blast was applied to the minerals used at the Devon and other ironworks, there was an evident improvement in the strength of the pig iron.

At that period too little importance was attached to the chemical constitution of pig iron to have prompted any one to ascertain, by actual examination, whether any change in this respect had been induced by heating the air, and at the present day it is, so far as my enquiries go, impossible to obtain specimens of hot and cold blast iron smelted from exactly the same materials.

The nearest approach I have been able to make to this is afforded by the assistance of my friend, Mr. Walter Williams, the well-known Staffordshire ironmaster, and even here, the specimens are far from being all that is to be desired.

The cold blast iron was the produce of the Staffordshire clay ironstone, smelted with South Staffordshire coke, and with the Dudley limestone as a flux. The hot blast iron was obtained from the same Staffordshire claystone, mixed with one-sixth North Staffordshire black band, and one-sixth red hæmatite. The limestone employed in this case was from Wales, but the fuel used was the same as in the cold blast furnace. There were thus two important

deviations from identity in the materials—the ore in the hot blast furnace contained one-third of hæmatite and black band, which were not present in that blown with cold air, and the limestone was different.

So far, however, as phosphorus is concerned, as the red ore is free from this ingredient, the sixth part of black band is the only source likely to bring any addition to this element, unless the flux from Wales is richer in P than that from Dudley.

Neither of these possible causes of contamination, however, have added, practically, either to the amount of phosphorus or sulphur contained in the hot blast iron, as may be seen from the following analyses, carefully done by my present assistant, Dr. Watson. Both samples were No. 3 in quality.

	Exp. 754. Cold blast.		Exp. 755. Hot blast.	
Fe	93·761	... ...	92·201	
C, graphite ...	3·062	3·405	2·568	3·161
combined ...	·343		·593	
Si	1·025	... ...	2·080	
S	·077	... ...	·065	
P	·663	... ...	·686	
Mn	·819	... ...	1·549	
	99·750		99·742	

In these experiments, there is a considerably larger quantity of Si in the iron produced by the hot, than by the cold blast furnace. In examining some of the analyses quoted in "Watts's Dictionary of Chemistry," the Si, in some cold blast iron, exceeds even the quantity given above; thus, in specimens of Dean Forest iron, made with cold air, 2·34 and 2·10 per cent. are given as the content of Si. Knowing from my own experience, however, how irregular the quantity of Si is in metal made in our own furnaces, blown with heated air, I was not disposed to attach much importance to this; nevertheless, other pigs of the same Staffordshire iron were sampled, and these, on trial, gave results which confirmed my opinion on the uncertainty as to the existence of Si in definite quantities.

Cold blast.		Hot blast.	
Exp. 756. No. 2 iron, Si%	1·446	Exp. 758. No. 2 iron, Si%	2·521
„ 757. „ „	1·294	„ 759. „ „	1·948

The only other notable difference between the two kinds of iron was the larger proportion of manganese in that made by hot blast. The presence of this substance was more likely to be an advantage than otherwise, but, to see whether its larger presence was accidental or not, further trials were made :—

Cold blast.		Hot blast.	
Exp. 760. No. 2 iron, Mn.%	1·060	Exp. 762. No. 2 iron, Mn%	1·726
„ 761. „ 4 „ „	·953	„ 763. „ 4 „ „	1·253

These numbers indicate that the metal, in question, occurs in larger quantity in hot blast iron, made of the minerals already specified, than it is found in cold blast iron, from a mixture of ore of a somewhat different character.

I have in vain sought to connect the alleged superiority in quality, said to be enjoyed by iron manufactured with cold air, with any freedom from those substances generally considered as affecting prejudicially the character of pig iron. Of course, in them, as in all iron, hot as well as cold blast, we are pretty safe in asserting that excessive quantities of Si, P, or S are hurtful, but on referring to a list of analyses in Bauerman's work on the "Metallurgy of Iron," it will be found that certain highly esteemed brands of cold blast iron appear to contain more of these substances than do others much less favourably known in the market.

Upon one occasion, the subject was made one of direct experiment at the Clarence Works. A furnace, about to be extinguished, was blown with cold air for a short time, the burthen of ironstone, of course, being reduced to meet the change of circumstances. The trial was made some years ago, and the pig iron not having been submitted to analysis, I cannot speak as to its composition, but so far as the quality of bar iron it afforded is concerned, I know positively there was not the slightest trace of improvement.

It is almost needless to observe, that a belief in the absence of any advantage in the quality of iron produced by one mode of manufacture or another does not involve any doubt as to the excellence of the produce of certain works which happen to be made by means of either; all that is intended to be conveyed by the general tenor of the present remarks is, that it scarcely has been satisfactorily proved that the excellence in question is really due to the temperature of the blast used in the smelting process.

I have been given to understand that, in some establishments,

making high-classed iron, when a furnace, worked with cold blast, is driven so as to produce above 90 tons a week, an unmistakeable deterioration in the quality of the bars obtained from pig iron manifests itself. Acceleration alone, in the speed of driving, may of itself give rise to an increase in the intensity of temperature evolved from a given quantity of carbon; but, at the same time, it is much more likely that the depreciation in quality, if it occurs, is due to a reduction in the actual heat of the hearth, which will be caused by a portion of the reduction being effected so low down in the furnace that the CO_2 dissolving C diminishes the weight of coke for combustion at the tuyeres, which, of course, will be followed by a lowering of temperature.

It might be inferred that when the problem to be solved was the mere determination of certain physical properties, there ought to be no difficulty in ascertaining the relative power of resistance possessed in every conceivable direction by iron, cast as well as wrought.

All this has been done, and well done, at a very early period by Fairbairn and Hodgkinson, at the request of the British Association for the advancement of Science. According to the report of these gentlemen, results were obtained of a somewhat unexpected nature; at all events, they certainly do not coincide with the relative estimation in which certain brands of iron were held, and continue to be held, in the market. The following figures are taken from one of their tables:—

	Tensile strength per square inch of section in tons.	Crushing strength per square inch of section in tons.
Low Moor No. 1, cold blast	5·667	27·003
„ No. 2, „	6·901	42·324
Bowling No. 2, „	6·032	33·507
Clyde iron No. 1, hot blast	7·198	40·535
„ No. 2, „	7·949	47·326
„ No. 3, „	10·477	47·338

The following table contains the data of different makes of pig iron manufactured by hot and cold blast, as determined by the same authorities as the preceding, in which the ratio between the two is given, cold blast being represented by 1000. From these it would

appear some irons are improved, and others are deteriorated in quality.

	Carron No. 2.	Devon No. 2.	Buffery No. 1.	Coed-Talon No. 2.	Carron No. 3.
Tensile strength	809	—	769	884	1,250
Compressive do.	1,020	—	925	1,012	1,156
Transverse do.	991	1,417	931	—	—
Power to resist impact	1,005	2,786	963	—	—
Transverse strength of inch square bars	973	1,199	942	—	—
Ultimate deflection do. in ins.	1,018	1,380	1,058	—	—
Modulus of elasticity ₱ sq. in.	931	991	893	—	—
Specific gravity	997	991	989	1,002	989

More recently, Mr. Kirkaldy has bestowed much attention on the strength of iron and steel, and the results of his investigations have been published.* From these the following numbers have been extracted to show that the more expensive irons do not exhibit a corresponding power of resistance. The specimens, Mr. Kirkaldy states, were obtained promiscuously from merchants' and engineers' stores, and in each case a rolled bar, one inch in diameter, was taken:—

Brand.	No. of expts. of each.	Breaking weight ₱ sq. in. of original area Lowest. lbs.	Highest. lbs.	Mean. lbs.
Low Moor	4	59,320	65,166	61,798
Bowling	4	58,678	65,701	62,404
Bradley	4	56,004	58,036	57,216
Govan (Scotch)	4	57,738	59,726	58,746
Govan (Scotch) B. Best	4	60,069	66,363	62,849

Later still, M. Knut Styffe, the Director of the Royal Technological Institute of Stockholm, by order of his Government, undertook a series of investigations, which are recorded in a book on the "Elasticity, Extensibility, and Tensile Strength of Iron and Steel."† In this book, information of temperatures at which fracture took place, and the carbon and phosphorus in the bars are given :—

* "Experiments on Wrought Iron and Steel," 1863.

† Translation by C. P. Sandberg. Murray, London, 1869.

Brand.	Per cent. Carbon.	Phosphorus.	Diameter of round bar. In.	Temp. of bar. F.	Breaking weight per sq. in. of original area. Tons.
Low Moor (cold blast)	·21	·068	·465	— 32	27·35
" "	"	"	"	+ 68	25·21
" "	"	"	"	+ 59	29·10
" "	"	"	"	+ 323	29·62
Middlesbro' (hot blast)	·07	·250	·581	— 40	27·44
" "	—	—	—	+ 57	25·81
" "	—	—	—	+ 60	23·58
" "	—	—	—	+ 59	26·46
" "	—	—	—	+ 318	31·12

The pages from which the preceding figures are extracted contain much information which would be out of place in such a work as the present. My object has not been to compare the relative value of different kinds of iron, but to show how difficult it appears to be to prove the resisting power of either cast or wrought iron by mere experiment.

It must be remembered that the researches which gave the results just quoted by no means represent the conditions of actual use. A cube or cylinder of cast iron may have a high tensile or compressive strength, but from excessive contraction in cooling in a large casting, may be in such an unequal state of tension as to break on concussion. In like manner, bar iron may, from causes our present state of knowledge does not enable us to explain, have great tensile strength, and yet be less able than others to resist those violent shocks, to which in many cases it is exposed.

All this goes to prove that it is long experience alone which secures, and properly secures, for any particular mark that preference which commands a high price in the market, and this position it necessarily maintains against the produce of any less well known manufacturer, who, nevertheless, may possibly turn out an article in all respects equal to that of his better known rival.

My intention in this section, however, is not with this aspect of the question. It is simply to express the opinion that no satisfactory proofs have been published to show that the use of hot blast is attended with hurtful effects on iron produced by its means, while many manufacturers, well known for the quality of their make

when cold blast alone was employed, have commenced the use of hot air without injury to the character of their iron; and further, that we have the evidence of authorities like Professor Tunner in favour of the view, that whether iron is smelted by heat intercepted in the upper part of the furnace, or by fresh heat added to the blast, the resulting temperature in the hearth, I maintain, being, in all probability, the same in each case, is immaterial so far as the nature of the product is concerned.

SECTION XLI.—ON THE THEORETICAL *MINIMUM* OF FUEL REQUIRED TO PRODUCE ONE TON OF PIG IRON.

Whether the actual amount of heat required in the production of a given quantity of pig iron has been stated with rigid precision in the present work or not, there is no doubt whatever that there is absorbed in the process a certain number of calories or heat units, and no more. The difficulty of defining what this quantity really is, arises, not from there being any variation or irregularity in the smelting operation itself under a given condition of things, but from the next to impossibility of correctly ascertaining the value of the factors which constitute the elements of the calculation.

Notwithstanding this uncertainty, I am of opinion that a sufficiently accurate estimate of the measure of heat required has been made to serve all practical purposes. The absorption of heat in the blast furnace, however, is not one of a simple character, *i.e.*, it means something more than a conversion of a known number of calories into their equivalent of fuel, by even the most accurate knowledge of the calorific power of such fuel, and its power to do a certain quantity of work implied by the mere absorption of heat. As we have seen, the full calorific power of the carbon which is burnt in the blast furnace has a restriction placed upon it by the chemical conditions attending the reduction of an oxide of iron.

Under these circumstances, it becomes necessary not only to ascertain how much heat is required for smelting iron, but we must know the precise extent to which we can look to our fuel for supplying that heat, and lying within this second branch of the enquiry, because, dependent upon it, is the subordinate one of how much of such heat must be obtained at the expense of burning fuel in the furnace, and how much may be derived from the less expensive source of having it communicated to, and conveyed by, the blast.

It has happened, upon more occasions than one, in recent discussions before the Iron and Steel Institute, that the question has been raised as to the minimum of fuel necessary for the production of a ton of iron, and what is the *maximum* useful temperature the air driven into the furnace can have.

No doubt much that can be said on these important questions has been already explained in these pages, but as the subject is one to which members of the Institute still address themselves, in their discussions, I have deemed it advisable to dedicate a distinct section to its consideration.

Before any attempt is made to ascertain how the necessary heat has to be commanded, we must agree on the exact quantity which is required, and to do this, an assumed condition of the fuel, of the atmosphere, and of the ironstone and limestone, must be taken as the basis of calculation.

For the estimate, the following will be adopted as forming the groundwork of the estimate :—

Durham coke, 100 parts, considered as consisting of—
Ash and sulphur 5 %, water 2·5 %, carbon 92·5 %.

One ton of iron will require—

Limest. 11 cwts., composed of 6·16 CaO 4·84 CO_2			
Ironstone of Cleveland, calcined—49 cwts. composed of 18·6 Fe 9·00 O, and 21·4 cwts. of earths, P.S., &c.			cwts.
Slag will weigh—ash from the quantity of coke used		...	1·10
CaO from limestone		...	6·16
Earths from ironstone	21·4		
Less bases, &c., taken up by pig iron, and evaporated in fume	·74	20·66	
			27·92

Applying these figures to the co-efficients of absorption already accepted, we have :—

		Cwts.		Units.
For Class I., No. 1.	Evaporation of H_2O in coke	·58 ×	540 =	312
„ „ 2.	Reduction of Fe_2O_3	18·60 ×	1,780 =	33,108
„ „ 3.	Carbon impregnation	·60 ×	2,400 =	1,440
„ „ 4.	Expulsion of CO_2 from CaO_3	11· ×	370 =	4,070
„ „ 5.	Decomposition of CO_2 in CaO_3 ... C	1·32 ×	3,200 =	4,224
„ „ 6.	Decomposition of H_2O in blast ... H	·05 ×	34,000 =	1,700
„ „ 7.	P_2O_5, SO_3, and SiO_2 reduced, say		=	3,500
„ „ 8.	Fusion of pig iron	20· ×	330 =	6,600
„ „ 9.	„ slag ...	27·92 ×	550 =	15,356
				70,310
Class II., No. 10.	Transmission through walls		3,600	
„ „ 11.	Carried off by tuyere water		1,800	
„ „ 12.	Expansion of blast, &c. ...		3,700	
				9,100
				79,410

This number, 79,410, is exclusive of the quantity of sensible heat carried off in the escaping gases, which varies, of course, with their temperature and weight, hence the absorption due from this cause will be provided for in the subsequent stages of the calculation.

In the data given above, the air is taken as somewhat drier than formerly (Section XXVIII.), and the P, S, and Si in the iron as the smallest quantity usually found in Cleveland pig metal.

It may be observed that the heat absorbed in the various steps of the process was deduced, in most cases, not alone from the direct experiment of different authorities, but the amount was checked by the heat evolved by the carbon in its ascertained state of oxidation, according to the data determined by the most accurate physicists. It will be seen the difference between the two sides of the accounts (*vide* Section XXVIII.) varied from 1,560 to 3,743

units, which, in 93,455, shows a discrepancy of only from 1·6 to 4 per cent. In the same section, a table, designated one of "constant requirements" was given, in which, when smelting Cleveland stone,

28·92 cwts. coke were used per ton of iron, and blast at 485°C.
22·32 „ „ „ 485°C.
22·00 „ „ „ 780°C.

Notwithstanding the different characters of these factors, the extreme variation in the heat absorption deduced from their values was within 1·9 per cent.

In the examinations of furnace workings, which have preceded, it was estimated that the weight of carbon per ton of iron as CO_2 in the gases could not exceed 6·58 cwts., this quantity representing the deoxidation and carbon-impregnation of 18·6 cwts. of Fe, which was taken as that existing in one ton of pig iron obtained from Cleveland stone.

Admitting, then, 6·58 cwts. to be the maximum proportion of carbon per ton of iron, to be found in the gases as CO_2, we must seek to ascertain to what extent a given volume of CO can abstract the necessary O from an oxide of iron required for its conversion into CO_2. The further we can carry this absorption, and retain the heat it generates, the less carbon will be needed in the form of CO, and the more extensively can we substitute heat obtained from the combustion of coke, by that injected into the furnace along with the blast.

On referring to the greatest quantity of CO_2, given in this work, as observed in furnace gases, we find the following figures:—

			Vols. CO_2 per 100 vols. CO.		
	Furnace.	Cubic feet.	Maximum.	Minimum.	Average.
Exp. 123.	Clarence ...	11,500 ...	50 ...	32 ...	44
„ 132.	Clarence ...	25,500 ...	45 ...	34 ...	40
„ 142.	Ferryhill ...	16,000 ...	46 ...	36 ...	40
„ 147.	Ferryhill ...	33,000 ...	43 ...	30 ...	36

In experiments 95 and 99, it was found that 100 vols. of CO, when mixed with 50 of CO_2, still possessed the power of reducing Cleveland stone, but it was so feeble that, in the former, in 5½ hours, only ·9 of the original oxygen (42·8) or 2·09 per cent., was removed; and in the latter, in 11½ hours, 4·3 (out of 42·8), or 10 per cent.; the

recorded temperature being 417°C. (782°F.) Such a temperature as 417°C. is higher than that which ought properly to be found in the escaping gases of a blast furnace, inasmuch as it would of itself involve a loss of heat which may be avoided. In the four trials just quoted it will be seen, however, that 45 to 50 vols. of CO_2 per 100 of CO have been observed in furnace gases, indicating, therefore, the power of CO to pass into the state of CO_2 to the extent of one-third its own volume, by absorbing O from Fe_2O_3. I possess no record of the actual temperature of the gases at the moment the samples containing this maximum of CO_2 were taken; indeed, this would be difficult, if not impossible, to ascertain, owing to the rapid fluctuations in the composition of the gases, and the slowness in the indications of any instrument which can be used for ascertaining the temperature. Judging, however, from a vast number of other experiments, it is highly improbable the average was below 330°C. (626°F.)

If a continuous stream of materials, mechanically and chemically speaking, the same, was flowing into a blast furnace, it is quite possible that the fluctuations, in respect to temperature and composition of the gases, would be removed. Practically, in furnaces, as they are at present constructed for taking off the gases, such a plan of charging could scarcely be pursued; nor am I prepared to admit that, were the uniformity spoken of attained, that the average in these respects would much differ from what it now is, but my present object is to show what the consumption of fuel might be, were it possible to maintain the gases at the maximum of oxygen saturation, and minimum of sensible heat, indicated in the instances just quoted.

For this estimate, 100 vols. of CO will be taken as being accompanied with 50 vols. of CO_2, or by weight 100 of CO to 78·3 of CO_2. In using ironstone perfectly dry, and at the temperature of the atmosphere, it will be assumed that the heat of the escaping gases is as low as 275°C. (527°F.)

It must, however, be understood, that this assumption of a maximum saturation of oxygen, and minimum quantity of sensible heat in the gases, is merely made use of as a basis of calculation, for I shall hereafter show that, although it is easy to maintain even a much higher proportion of CO_2 than 50 vols. to 100 of CO in the gases, and it is also within our power to cool them to 275°C., it is, in

my opinion, quite impossible to command these two conditions simultaneously, and I shall also give experimental evidence to prove that as we gain by the one, we lose by the other, and *vice versa*. It must also be borne in mind that with such a large quantity of CO_2 in the gases (50 vols. to 100 CO), it required a temperature (Exps. 95 and 99) of 417°C. (782°F.) to remove the small proportion of oxygen just mentioned. At 275°, the temperature to be assumed in our calculation, it must be considered that the gases are not only practically, but are physically, saturated with oxygen, so far as they can be, when calcined Cleveland stone is the source of this element.

To proceed with the estimate, 6·58 cwts. of carbon which pass into the state of CO_2 for each ton of iron in the manner supposed is equal to 24·13 CO_2, and therefore affording, by oxidation, 52,640 units.

The actual weight of the gases containing 6·58 cwts. of C as CO_2, and consisting of CO and CO_2 in the proportion of 100 to 78·3 will be—

CO., 30·85 cwts. containing	13·22 cwts.	C
CO_2 24·13 „ do.	6·58 „	„
54·98 containing C	19·80 „	„
Of which the limestone supplied ...	1·32 „	„
Leaving to be supplied by the coke ...	18·48 „	„
Carbon taken up by the iron	·60 „	„
Total carbon in the gases derived from coke	19·08 „	„

and 19·04 of carbon is equal to 20·62 cwts. of coke containing 92·5 per cent of this element.

The figures just given will enable us to proceed to compare the heat evolution with its appropriation upon the data already set forth, as well as to determine the temperature of the blast.

The total oxygen contained in the above-named quantities of CO and CO_2 is 17·55 in the one, and 17·63 in the other, or a total of 35·18 cwts.; hence, it would appear that the oxygen is equally divided between its combination of CO and CO_2.

From the total oxygen in gases, viz., ...		35·18 cwts.	
Deduct that derived from the Fe_2O_3, P_2O_5, SiO_2, and SO_3 in the ore, say	9·00		
Deduct that derived from the limestone	3·52		
Do. do. moisture in blast	·40		
		12·92	„
Leaving the blast to supply		22·26	„
Add weight of nitrogen accompanying this O		74·52	„
Moisture		·45	„
Weight of blast		97·23	„
Weight of gases—Blast	97·23		
O from ore, limestone and H_2O	12·92		
C in gases	19·80		
H_2O from coke ...	·50		
		130·45	„

The total number of calories actually required will be those given in a previous page		79,410
The total number in 130·24 cwts., gases at a temperature of 275°C. 130·24 cwts. × 275°C. × ·24SH		8,610
		88,020
The heat evolved will be as follows:—		
C to CO ... 13·22 cwts.		
Less than in limestone 1·32 „		
11·90 × 2,400 =	28,560	
C to CO_2 ... 6·58 × 8,000 =	52,640	
18·48		81,200
Left to be supplied by the blast ...		6,820

and $\frac{6{,}820 \text{ units}}{97{\cdot}23 \text{ cwts.} \times {\cdot}237 \text{ SH}} = 297°\text{C. } (527°\text{F.})$

The calculation works out to a lower temperature in the blast than any ironmaster knows will suffice in practice, when using so small a quantity of coke as 20·58 cwts. This is partly owing to the fact that the gases are taken below the usual temperature at

which they leave the furnace, and partly due to the circumstance that they do not generally contain quite the full equivalent of CO_2.

These two corrections would bring up the temperature required in the air, but they do not, in any way, affect the weight of coke consumed, which, I much doubt, under the conditions assumed, will ever be reduced practically below 20½ cwts. per ton, and, to cover those irregularities so frequently mentioned upon other occasions, it is rather to be expected that for a ton of No. 3 iron it will more frequently be 21, or perhaps nearer 21½ cwts.

By the erection of enormous furnaces, and the adaptation of heating apparatus of immense power, hopes have been expressed of reducing the consumption of coke to 18, or indeed 17 cwt. per ton, of iron obtained from Cleveland stone. Now, the effect of this would be, that the CO_2, generated in the zone of reduction, would bear the ratio of about 96 parts, by weight, for each 100 of CO.* I do not pretend that a mixture consisting even of equal weights of CO and CO_2 (100 vols. CO to 64 CO_2) possesses no reducing power, but it must be very faint, and will require a higher temperature than that usually found in the gases leaving a blast furnace. This is inferred from the experiments referred to at the beginning of this section, seeing that pure CO only commences to exhibit marked action on Cleveland stone at 210°C. (410°F.)—*Vide* Exp. 17.

It does appear, however, that there is a certain amount of inconsistency in the simultaneous adoption of very large furnaces, and very high temperature of blast. The increase of dimensions afforded a reasonable prospect of permitting the gases to part with more of their sensible heat, and of becoming more thoroughly saturated with oxygen before leaving the throat, than happens when smaller dimensions are adhered to; and these actions are necessarily attended with a saving of fuel. When this augmentation in size is practicable, and very large capacity is efficacious in economizing coke, it is unnecessary to raise the temperature of the blast, inasmuch as the quantity of heat evolved from such a state of oxidation of carbon as I have supposed in the estimate, viz., 6·58 parts to CO_2 and 13·18 to CO, is equal to giving a ton of iron, as we have just

* *Vide* Table, Section XXXII., on Composition of Gases, using different quantities of coke.

seen, with a blast of very moderate temperature, viz., 297°C. (527°F.)

It may, no doubt, be argued that further action, by a gas on an oxide of iron still possessing reducing properties, ceases, because it is cooled below that point where deoxidation is effected, and that, in consequence, it is reasonable to expect that raising the temperature of the blast would, by a general elevation of the heat of the gaseous and solid contents of the furnace, enable reduction to be effected by a mixture of CO and CO_2, which, at lower temperatures, is inert.

Of course, such a procedure would mean that the escaping gases were leaving the furnace in a more highly heated condition than before, and, hence, one advantage accruing from an enlargement of size would be at once defeated. This is a state of things, however, that would be unproductive of any real gain, *i.e.*, it would be useless to add a given number of heat units at the bottom of the furnace if the same number escaped at the top. The additional heat, therefore, to have any value, must have additional work to perform by adding a greater load of ironstone to the coke.

Inasmuch, however, as very much larger proportions of CO_2 than 50 of this gas to 100 vols. of CO have been shown to possess, under certain circumstances, well marked powers of deoxidizing Cleveland stone, it may be well to consider the nature of those circumstances with a view to see how far they can be applied to the blast furnace, when smelting this ore with coke.

In Exp. 81, CO was entirely converted into CO_2 by being passed slowly over a large excess of calcined Cleveland stone, at a temperature a little above that of melting zinc. The Fe_2O_3, however, only lost 5·25 per cent. of its O.

In Exp. 82, 100 vols. CO and 600 vols. CO_2 at a low red heat removed 5·8 per cent of the O from Cleveland calcined ore.

In Exp. 84, 100 vols. CO and 220 vols. CO_2 at a heat just visibly red absorbed 11·7 per cent. of the O in Cleveland stone.

In Exp. 85, equal volumes of CO and CO_2 formed stable compounds with various ores, at a red heat. They were reduced to Fe O, and spongy metallic iron exposed to this mixture of gases at the same time, absorbed oxygen and became Fe O.

Now, there is no doubt the furnace itself may be made to imitate the action just mentioned, *i.e.*, the issuing gases may contain a

very much larger proportion of CO_2, than that expressed by the ratio of 50 vols. to 100 of CO.

Exp. 764. Immediately after charging into the Wear furnace (17,500 cubic feet) 25 cwts. of coke, 12 cwts. of limestone, and 54 cwts. of calcined Cleveland stone, in the order in which they are mentioned, the gases were found to consist of

CO_2	8·8	CO_2	30·66 vols. for 100 vols. CO, or
CO	28·7	„	48·06 parts by weight to 100 CO.
H	1·1		
N	61·4		
	100 vols.		

All charging was now discontinued, and the gases were sampled at intervals of 20 minutes, and afforded the following results:—

		CO_2	CO	H	N	Vols.	100 CO = CO_2 by Vols.	by Weight
Exp. 765.	end 20″.	10·7	29·2	3·3	56·8	=100	36·64	57·38
„ 766.	„ 40″.	12·3	25·2	3·8	58·7	=100	48·81	76·44
„ 767.	„ 60″.	22·2	16·9	2·1	58·8	=100	131·36	205.89

To verify the correctness of these numbers, Exps. 766 and 767 were repeated.

Now, really what takes place under such conditions as those just described, I take it, is this. After charging, any soft coke is immediately attacked, and C is dissolved at the expense of CO_2. At the Wear Works, this happens in a more striking way, perhaps, than usual, owing to the coal used there giving a softer coke. This action, however, ceases in time, and the CO_2 produced by deoxidation, not passing through any fuel, owing to the order in which the materials were charged, begins to increase as is seen in Exp. 764 and 765, in which the ratio has risen from 30·66 to 36·64 vols. This continues, and, by the end of the hour, it has become 131·36 vols., or above two and a-half times that which was adopted as the basis of the calculation to obtain the theoretical *minimum* of coke.

A great deal, however, of the heat evolved by the extraordinary proportion of CO_2 is lost, for being generated so near the point of exit, it is carried away in the escaping gases, as may be seen by the following observations:—

	Clarence.	cubic ft.	Temp. °F.	Ceased charging during h. m.	Temp. °F.	Rise. °F.
Exp. 768.	No. 4 fur.,	25,500	579	1 26	816	237
„ 769.	„	„	564	1 20	814	250
„ 770.	„	„	593	1 23	797	204
„ 771.	„	„	586	1 40	788	202
„ 772.	No. 5 fur.,	25,500	608	1 30	844	236
„ 773.	„	„	644	1 20	834	190
„ 774.	„	„	586	2 30	887	301
„ 775.	„	„	629	1 42	867	238
Average rise	...	...	...	1 36		232=129°C.

Now the ordinary composition of the gases of the Wear furnace, when working upon the burden mentioned above was, by weight,

(*V.* Exp. 536) CO_2 14·9, CO 28·2 } = 52·8 parts by weight of CO_2 to 100 CO
N 56·9
100·

And, in round numbers, the calories evolved by burning the fuel used per ton of iron, viz., 23·5 cwts. (*v.* Exp. 536) would, when the gases were emitted, containing CO_2 to CO as 205 to 100, be above 30,000 more than when the oxides of carbon were as 52·8 to 100.

Practically, however, any heat thus evolved and afterwards absorbed is in part entirely wasted, because the moment charging is resumed the accumulation enables the highly-heated CO_2 to act more vigorously on the freshly added coke, and, that coke acts quickly in this way may be inferred from the following line of argument.

In Exp. 751, data were given, which showed, bulk for bulk, ironstone possessed twice the power of coke in intercepting heat when a current of hot air was blown through it, there being under the circumstances of the trial no chemical action. Now, as ironstone is about double the weight of coke, it follows that weight for weight their heat-intercepting powers are about equal. It may, therefore, be expected that apart from chemical action, if 24

cwts. of coke were introduced into a furnace it would affect the temperature of the gases by simple refrigeration to the extent of something like one-half the extent of that of 50 cwts. of ironstone, including its flux.

Exp. 776. Twenty-five observations were made on the temperature of the gases five minutes after charging 24 cwts. of coke. The fall varied considerably, but the average was 38°F. (21°C.)

Exp. 777. A similar number of trials was made after charging 50 cwts. of mine, &c. Here, too, the variation was great, but the average cooling amounted to only 23°F. (13°C.), also observed five minutes after charging.

Now, under no circumstances can the introduction of coke into the reducing zone be accompanied by an evolution of heat. Undoubtedly, it is otherwise to some extent, but not a large one with ironstone; but however this may be, five minutes would not suffice to bring it up to the necessary temperature to induce strong chemical action; so that, in the twenty-five experiments just described, we may regard it as occupying the same neutral position it did when hot air was blown through it. Admitting this, as regards the ironstone, there seems no alternative but to ascribe the increased rate of cooling exercised by the coke in the blast furnace to chemical action, *i.e.*, the high temperature of the gases expends itself by causing CO_2 to act on the carbon.

I proceeded to examine the correctness of this supposition by the following series of experiments. The fall of temperature was ascertained to be as follows, after the dinner time, during which, charging had been discontinued :—

	Temp. after dinner.	After charging three rounds, weighing 403 cwts. of coke, mine, and flux.	Time occupied. h. m.	Fall.
Exp. 778.	... 816°F.	... 572°F.	... 1 10	... 244°F.
„ 779.	... 816	... 552	... 1 30	... 264
„ 780.	... 797	... 636	... 0 50	... 161
„ 781.	... 788	... 552	... 1 0	... 236
„ 782.	... 834	... 593	... 1 0	... 241
„ 783.	... 834	... 629	... 1 40	... 205
„ 784.	... 887	... 617	... 0 50	... 270
„ 785.	... 867	... 624	... 1 0	... 243
		Average fall		... 233 =129°C.

So that the gases have fallen in temperature, after 403 cwts. were introduced to fill the furnace again, almost exactly what they had risen while charging was discontinued.

The next step was to ascertain the nature of the change which had taken place in the composition of the gases, and this is set forth in the following analyses:—

		CO_2.	CO.	H.	N.	Vols.
Exp. 786.	After ceasing to charge	8·8	28·7	1·1	61·4	=100
„ 787.	Before starting to charge after an interval of 1¼ hr.	22·2	16·9	2·1	58·8	=100
„ 788.	After first round	10·9	28·6	3·2	57·3	=100
„ 789.	„ third „	8·3	30·4	2·2	59·1	=100
„ 790.	„ fourth „	11·3	23·8	4·0	60·9	=100

In order to prove how immediately the high temperature, acquired during the dinner hour, causes the CO_2 to act on the coke, the following experiments were performed at the Wear furnace (17,500 cubic feet).

	Hour.	Charged.	CO_2.	CO.	H.	N.	= Vols.	Vols. CO_2 per 100 CO.
Exp. 791.	11·40	... ...	11·6	28·1	1·8	58·5	= 100	41
„ 792.	12·5	Charged 1 round coke, ironstone, &c., furnace full	10·7	not ascertained.				
„ 793.	12·30	... ...	11·7	do.				
„ 794.	12·55	... ...	19·1	18·3	0·2	62·4	= 100	105
	1·10	Charged 52 cwt. coke.						
„ 795.	1·12	No further charging	13·1	22·7	2·7	61·5	= 100	58
„ 796.	1·28	do.	11·1	25·2	1·3	62·4	= 100	44
„ 797.	2·10	do.	12·7	23·5	2·0	61·8	= 100	54
„ 798.	2·55	do.	22·7	17·8	—	59·5	= 100	128
„ 799.	3·40	do.	15·8	16·4	1·5	66·3	= 100	96
„ 800.	4·5	do.	11·8	26·7	1·2	60·3	= 100	44

In the above experiments, the furnace, on being filled up with the ordinary round, viz., coke 26 cwts., mine 54 cwts., limestone 12 cwts., the gases exhibit their ordinary composition. Nothing was filled during 1 hour 5 minutes, by which time the CO_2 had risen from 41 vols. to 105 vols. per 100 CO. Two rounds, weighing 52 cwts. coke (Exp. 795), were then let at once into the furnace, and immediately after the CO_2 fell to 58 vols., and in 18 minutes, to 44 vols. per 100 of CO. The CO_2 now began to rise again, and reached, in Exp. 798, 128 vols. per 100 of CO. No more ironstone being introduced, the CO_2 now began to fall off in quantity, and in 3 hours 55 minutes, had fallen to 44 vols. per 100 of CO.

To ascertain what the temperature really was, which sufficed for this speedy action of coke on CO_2, the following trials were instituted, also at Wear furnace.

	Hour.			CO_2	CO	H	N	Vols.	CO_2 per 100 vols. CO	Temp.
Exp. 801.	12	...	...	12·5	... 26·4	... 3·8	... 57·3	= 100	... 47·3	
„ 802.	12·13	...	...	12·0	not ascertained.					800F.
	12·20	let in 26 cwt. coke								
„ 803.	12·23	...	...	...	...	...	...	...		625F.
„ 804.	12·30	...	...	10·7	... 30·6	... 1·3	... 57·4	= 100	... 34·9	
„ 805.	12·45	...	...	8·4	not ascertained. probably 30·					
„ 806.	1·35	...	...	16·7	... 21·0	... 1·5	... 60·8	= 100	... 79·5	... 1025F.

After Exp. 802, when the coke was introduced the temperature of the gases would probably be 850°F., and the CO_2 to CO most likely as 50 to 100 vols. In three minutes after the coke entered the furnace, the temperature of the gases fell to 625°F., and they immediately afterwards contained CO_2 and CO in the ratio of probably 30 vols. to 100.

In this way, it will be perceived that there is a constant struggle between the formation of CO_2, accompanied by high temperature and the reduction of the CO_2 thus generated, back again to CO, a which latter change is, of course, effected at the expense of heat. Between these two extremes there is a middle course in which time is an important element, for the quantity of CO_2 formed, and its attendant heat, will depend upon the relative rapidity with which CO can absorb O from the Fe_2O_3 under treatment, and that at which the resulting CO_2 takes up a fresh equivalent of C. In the case of Cleveland stone the mean of the two conflicts, in my opinion, is generally reached even before the CO_2 exists in the proportions which constitute the basis of the calculation just given, viz., 50 vols. of this gas to 100 vols. of CO, and when the temperature of the escaping gases consequent upon this proportion of CO_2 is about 330°C. (626°F.) I will hereafter give a remarkable instance of a very different rate of fuel consumption from that obtainable when the ironstone of Cleveland is the ore used in the blast furnace, and an attempt will be made to explain the cause of this modification in the progress of the action.

If, then, accompanying a given quantity of heat required for the production of a ton of pig iron, a certain quantity of CO must be present, it follows as a matter of course that any heat contributed

by that contained in the blast will be useless, which when it is added to that generated by the formation of the CO rendered necessary by the nature of the process, the sum of the two exceeds that shown to be required. I have endeavoured to prove what becomes of this surplus of heat, viz., that it passes off in the escaping gases, or it is expended in the CO_2, formed in the upper zone of the furnace, absorbing C.

The second branch of the enquiry, viz., the *maximum* temperature the blast ought to have to permit its profitable application, is dependent entirely on the extent to which the permanent state of oxidation of CO to CO_2 is maintained. If it can be carried to such a point that the whole of the CO_2 due to deoxidation and carbon impregnation escapes as such, and that 100 vols. of CO can restrain the oxidizing influence of 50 vols. CO_2, then I have shown with the escaping gases at a temperature of 275°C. the air only requires to be heated to 297°C. (527°F.) to supply the deficiency of heat.

To effect this, however, the whole of the conditions must be favourable in the highest degree. The coke must be of that quality as to resist the power of heated CO_2 to dissolve it, and the gases must be prevented acquiring a temperature beyond 275°C. All this is attended with much difficulty, so much, indeed, that it far oftener happens that the total C escaping is not much above 6·0 cwts. as CO_2, and the CO_2 to CO is as 40 or 45 vols. to 100, or as 62·7 to 100 by weight, with a temperature of 330°C.

Now the difference between such a state of working, and that which has been hypothetically assumed as the basis of the calculation which brought out 20·62 cwts., burnt with the blast at 297°C. as being the quantity of coke required to produce one ton of iron, will be somewhat as follows. There will be a loss of ·58 cwts. of carbon burnt to CO instead of CO_2 equal to (·58 × 5,600) 3,248 calories, and the gases escaping at 330°C., instead of 275°, will represent about 1,700 units, making together, say 4,900 to 5,000 units. If the coke remained as it was, viz., 20·62 cwts., there would be nearly 5,000 units to be conveyed by 97·23 cwts. of blast, which represents an increase of temperature of about 190°C., making the total 502°C. (935°F). In practice, however, the diminution of CO_2 in the gases affects the quantity of carbon to be burnt at the tuyeres where at all events, the heat evolved is more readily rendered available by interception, hence the actual loss arising from the

causes now under consideration, is more generally to be met partly by a little more coke as well as by an increase in the temperature of the blast.

The manner in which defects of so varying a character have to be provided for, scarcely admits of very precise estimation. It must, in consequence, rather be the result of general experience than that of any formula of figures. Regarded in this way, I would give it as my own opinion that taking the ordinary run of Durham coke and Cleveland ironstone, the iron master who produces a ton of No. 3 iron with 21½ cwts., with the blast heated to 500°C. (932°F.) may consider himself as working very closely up to those limits of economy which are prescribed by the nature of the materials he is operating upon.

Independently of any increase of temperature in the upper portion of the furnace, the use of the hot blast introduces a change in the relation between the solid and gaseous contents, which will have the effect of accelerating the tendency towards an equalization of temperature of the two. By this action the ore is more speedily heated, and the gases, in consequence, are more quickly saturated with oxygen gas. This arises from the longer retention in the furnace of the carbonic oxide evolved by the combustion of a given weight of coke, and this happens in the following way:—

Let us imagine that a furnace of 6,000 cubic feet has conveyed into it, by means of the hot blast, 14,400 cwt. heat units per ton of iron, over and above the number it would receive were the air driven into it at the temperature of the atmosphere. This is equal to the heat from 6 cwts. of carbon burnt to CO, which C can therefore at once be withdrawn from the fuel introduced with the charges.

This quantity of carbon represents in resulting gases (C, 6; O, 8; N, 26·8) 38·8 cwts.

This is equivalent to a reduction of nearly 10 per cent. in the volume of the gases flowing up through the contents of a furnace using originally 60 cwts. of coke per ton of iron. During the time, therefore, each cwt. of carbon is engaged in fusing the iron and slag in the hearth, while in the act of being converted into carbonic oxide, the CO thus formed is retained, by the diminution in its volume, one-tenth longer period in the furnace, and by so much its

contact with the materials it has to heat and to reduce is prolonged. This effects a further saving of fuel, and, in consequence, a further reduction in the volume of gas is accompanied again by an addition to the time of retention of this gas in the furnace. This is continued until the fuel is diminished in quantity, as far as a furnace of the supposed dimensions is capable of producing a ton of iron, which is not reached until the gases in bulk are a mere trifle above one-half what they were when the blast consisted of cold air, instead of with the supposed addition of the 14,400 units in question.

It is clear, under such circumstances, the reducing gases will be twice as long in contact with the ore they have to reduce, and with the materials they have to heat, as when cold blast is employed.

That it is time alone which effects the change, and no mysterious virtue in the heat of the blast, is proved, I submit, beyond all doubt, by the fact that precisely the same results, in point of fuel consumed, are obtained by a suitable enlargement in the dimensions of the furnace, by which prolonged contact between the gases and solids is, in like manner, secured.

Before concluding this section on the economy of fuel, I would briefly notice a plan recommended by Mr. C. Schinz, in his work on the blast furnace,* and which he has patented under the title of "A process for partly eliminating the nitrogen in the products of combustion."

Half the schemes intended to improve the smelting of iron are propounded by persons who, neither by practice nor study, have endeavoured to make themselves acquainted with the principles upon which it is dependent. To this class, Mr. C. Schinz is a striking exception, for he has taken infinite pains to convince himself of the soundness of his project, and yet I entertain little hope of its sharing a different fate from many of its less studied predecessors.

The plan, in reality, consists of forcing carbonic oxide, obtained in one or two different ways, into the blast furnace; but, apparently, the one, preferred by the inventor, consists in heating refuse coke and carbonate of lime in retorts similar to those employed in a gas manufactory.

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* "Dokumente betreffend den Hohofen."

I am at a loss to know from what quarter refuse coke has to be obtained, in sufficient quantity, to constitute an important saving in the fuel consumed in iron smelting; but, omitting this difficulty, I cannot see how an elimination of nitrogen, partial or entire, can produce any notable economy in the quantity of fuel required for the process. The production of CO, containing the necessary quantity of carbon, would require an enormous establishment, and a great expenditure in labour and in heat, exceeding the value of its equivalent weight in coke, and, after all, we obtain a fuel, CO, which the nature of the process would not permit us to oxidize at the tuyeres. Independently of all this, calculation would show that the absorption of heat in decomposing carbonate of lime, and resolving its CO_2 into CO, is so great as to present an insuperable barrier to our being able, profitably, to avail ourselves of Mr. C. Schinz's proposal.

SECTION XLII.—SUPPLEMENTARY REMARKS ON THE ACTION OF THE BLAST FURNACE, IN CONNECTION WITH ITS DIMENSIONS, AND THE USE OF SUPER-HEATED AIR.

In an operation, involving so many disturbing causes as the smelting of iron, it cannot be a matter of surprise that there should, in the minds of even the most observant and experienced men, occur some differences of opinion. These differences can only be reconciled by a continuous system of observation and experiment, and as certain branches of the question have only in recent times occupied a proper amount of attention at the hands of British ironmasters, it is a subject which, in reality, may be said only to have begun to make a certain amount of progress, in this country, within the last year or two. Having arrived at the concluding portion of my labours, I have deemed it desirable, before closing them, to add a chapter, which should contain, if needful, any modification of those views directly affecting the main object of my enquiry when these researches were first undertaken.

The conclusion to which I have arrived, viz., that the point of economy of fuel, attained by the Cleveland smelters in their gigantic furnaces, fed with highly-heated air, had almost reached its limit, occupied, only very recently, the attention of the members of two societies, well qualified to discuss it—I mean, the Institution of Civil Engineers, and the Iron and Steel Institute.* Upon those occasions, it was maintained, that there was still room for improvement by a further enlargement of our furnaces, provided we altered their shape, and that the utmost practicable intensity of heat should be conferred upon our blast, if we wished to reduce the consumption of coke to the lowest point.

Looking at the present high price of this article, no one will doubt the earnestness of the wish of its largest consumers to see the quantity required for their work reduced to a minimum; but this desire may lead those who entertain it to needless expense, and it therefore becomes more necessary than ever that the iron-furnace owner, interested, as he is in the subject, should consider it, in all its bearings, in reference to his own process.

Among those who have studied the application of super-heated air, Mr. Thomas Whitwell occupies, deservedly, a very conspicuous place, from his personal labours in adapting it to furnaces of several sizes, and from having observed its effects upon different kinds of ore. The experience thus gained, Mr. Whitwell has not concealed from his colleagues in the iron trade; and I would therefore claim attention to the last of his communications to the Iron and Steel Institute, read before its members at their meeting in Dudley.†

This paper, to some extent, is a reply to certain statements I had made in Section XXXI., on the results obtained by the use of super-heated air to the Consett furnaces, 55 feet high, engaged in smelting a mixture of hæmatite and Cleveland stone. It concludes with asserting:—

1st. "That the increase in production in the furnace, No. IV., at Consett, is directly in proportion to the increase in the amount of blast thrown into the furnace, and not consequent on the reduction of temperature.

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* *Vide* "Minutes of Proceedings of Institution of Civil Engineers, 1871," and "Journal of Iron and Steel Institute, November, 1871."

† "Further Results from the use of the Hot-Blast Fire-brick Stoves."—"Journal of the Iron and Steel Institute, Vol. II., p. 217."

2nd. "That other things, such as the action of the materials in charging, and form of furnace being equal, a regularity of quality in the iron is in no degree incompatible with a high degree of temperature in the blast.

3rd. "That in the two furnaces at Consett, under consideration, although there is a great difference in the internal form and capacity, yet no reduction of temperature in the blast has been attended with economy; but that, in both cases, a reduction of 200°F. in the temperature of the blast, has been attended by an increase of upwards of 2 cwts. in the consumption of coke per ton of iron."

By the favour of Mr. Jenkins and the Directors of the Consett Iron Company, Limited, I have had an opportunity of examining the statements from which these conclusions are drawn, and, which, according to Mr. Whitwell, "prove, beyond all doubt, that *reduction in temperature*, at Consett, so far as coke is concerned, has been followed by *increased consumption*."

Now, I am not prepared to deny—on the contrary, I have, on more occasions than one admitted—that the use of superheated air, at Consett, may have been very beneficial, looking at the character of minerals smelted in such furnaces as those at this establishment. I would further take this opportunity of stating that to the principle of the fire-brick stove, I have not only no objection, but on the contrary, I believe, for durability, for economy of fuel, and for opposing the least possible amount of resistance to the blast, it has, taken as a whole, no equal. For the present state of perfection to which this form of hot-air apparatus has been brought, we are entirely indebted to the perseverance and ingenuity of Mr. E. A. Cowper, Mr. Charles Cochrane, and Mr. Thomas Whitwell. My business, however, is with the chemical effect alone of superheated air in the blast furnace. I am quite ready to leave the question of mechanical appliances, and cost of construction of this invention, to engineers, but it is quite impossible, consistently with the enquiry I have, in undertaking the present work, proposed to myself, to avoid examining, as well as I am able, the advantages or disadvantages of the use of air at more elevated temperatures. The designers of the fire-brick stove ought to rest satisfied with recommending it for the purpose of heating the blast as high as chemistry, and, I believe, as experience show to be useful; and not confine themselves to urging its adoption, merely

because it possesses, to an extent far beyond the reach of iron stoves, the power of superheating air.

If the Exps. 33, 35, 43, and 44, are referred to, it will be seen that when hæmatite and Cleveland stone were exposed to the reducing action of CO, or of mixtures of CO and CO_2, the former always gave up its oxygen, and became charged with deposited carbon much more speedily than calcined Cleveland stone.

	Time of exposure.	Temperature.	Gas.	Lost of original O per cent. Hæma- tite.	Calc. Clevel'd.
Exps. 43 and 44.	7½ hrs. ...	410°C.(770°F.)	pure CO	...57·4	...20·7
„ 33 and 35.	6 „ quick current.	410°C.(770°F.)	„	...70·9	...50·6

In each case, the two descriptions of ore were exposed simultaneously in the lead bath arrangement.

This difference in susceptibility to reduction leads us to the inference that a much smaller furnace may suffice for smelting the one than the other of these minerals, for reasons already given in a previous section. It is, perhaps, not very easy to adduce absolute proof as to the cause of unnecessary height in a furnace actually being prejudicial. It is, however, not difficult to suppose that the ore itself, being in small pieces, naturally, or split up into the coarse powder, attending its impregnation by carbon, may assume such a position in relation to the coke as to permit the formation of channels, and, in consequence, the too ready exit of the reducing gases. This, however, is certain, the Consett Company built a furnace, about 70 feet high, to smelt the mixture of hæmatite and Cleveland stone, treated so successfully in those of 55 feet furnished with the fire-brick stoves, and were compelled to reduce its dimensions.

We have, further, the admitted fact, that when the Consett Iron Company smelted this mixture of minerals in a 55 feet furnace, with air heated only to 454°C. (850°F.) (*vide* Section XXVIII.), the consumption of coke was more than 4 cwt. in excess of that used when the blast had a temperature of 718°C. (1,324°F.) These circumstances render it impossible to deny the importance of the service which Mr. Whitwell has rendered in this particular instance.

It would, indeed, appear that there exists some difficulty in the treatment of these rich Lancashire ores in furnaces of the more

modern dimensions, which may require further examination and study; but, at the same time, even those of the lesser construction scarcely enable this mineral to be smelted with as small an amount of fuel as one might expect.

At Barrow, for example, some of the furnaces are 46 feet, and others, 56 feet high. I have been given to understand that the consumption of coke, per ton of iron, was as small in those of the esser description as in the larger. More recently, at the same establishment, a furnace, having a height of 75 feet, has been erected, and so unmanageable did it prove, that 14 feet have been removed from the top, so that it is now only 61 feet high, and is working satisfactorily.

At Askham, again, we have a furnace, 67 feet high, with a capacity of 13,100 cubic feet, which, from a paper by Mr. W. Crossley, read before the Institution of Mechanical Engineers,* does not appear to be performing its duty as advantageously as those at Barrow, containing 9,000 to 10,000 cubic feet.

None of these furnaces, however, afford such good results as those in the Cleveland district, having regard to the superior richness of the Lancashire ore. Thus, according to the data supplied by Mr. Crossley, which contain the most ample information we have yet received on the treatment of this description of mineral, the heat, compared with that absorbed in the smelting of Cleveland ironstone is as follows:—

Less $CaCO_3$ to decompose (9, instead of 12 cwts.)	$3 \times$	370 =	1,110
„ CO_2 from $CaCO_3$, dissolving C ...	$\cdot 36 \times$	3,200 =	1,152
„ P_2O_5 to decompose		=	1,500
„ slag to fuse (15 cwts., instead of 30 cwts.)	$15 \times$	550 =	8,250
Total less cwt. calories required, per ton of iron, from Lancashire than from Cleveland ore			12,012

This number of calories evolved, when using a well-heated blast, say, 485°C. (905°F.), at the tuyeres, is equal to about 4 cwts. of coke.

Now, taking 21½ cwts. to 22 cwts. of coke to represent the consumption, on the banks of the Tees, for each ton of No. 3, we

* *Vide* Proceedings, July, 1871.

have 17½ to 18 cwts. as the quantity which ought to be that for obtaining the same quality of metal on the West coast, which is, I understand, below that generally heard of in that district.

Now, in the Consett furnace, No. 4, when the minerals used are employed in such proportions that one half the iron is due to hæmatite, and the other half is due to Cleveland stone, the average over 14 months is about 19½ cwts. of coke for metal, a shade under No. 4. If we take that due to the Yorkshire ironstone at 20½ cwts. per ton of No. 4 iron, we have 18½ cwts. left for the production of the metal from the Lancashire mineral; and, so far, the Whitwell stoves have done for hæmatite, when mixed with Cleveland stone, that which, when using the former alone, has, it seems, not always been accomplished in the Cumberland and Lancashire furnaces.

Referring, again, to Mr. Crossley's paper: as the West country hæmatites are, according to my experiments, more susceptible to the action of CO, it is remarkable how poor the gases from the Askham furnaces appear to be in CO_2, which gas, of course, is the indication of efficient working.

Analysis of Askham escaping gases, using 22¾ cwts. coke.

N ...	54·51 vols.	...	52·59 by weight.	
CO ...	34·97 „	...	33·80	„
CO_2...	8·36 „	...	13·47	„
H ...	2·16 „	...	·14	„
	100·00 „		100·00	„

100 CO=CO_2 24· by vol. 39·84 by weight.

When this comparatively small quantity of carbon, escaping as CO_2, is made the basis of calculating the heat development, it is easy to find why—although 12,000 cwts. calories less are required in smelting Lancashire ore—no saving in fuel accompanies this easier rate of reduction. Estimated upon a ton of iron, Mr. Crossley mentions that 4·36 cwts. of C only (instead of 6·5 cwts.) escape as CO_2, being thus 2·14 cwts. less than are found in the furnace gases, near Middlesbrough. The loss of heat from this cause is (2·14 × 5,600) 11,984 units.

When it is remembered in the experiments described in these pages, that hæmatite ore is more easily reduced than that of the Cleveland Hills, one is scarcely prepared for the less perfect mode of working just alluded to. It happens, however, so uniformly, and

this in furnaces of different sizes, that the conclusion seems irresistible that it is due to some property inherent in the ore itself. The actual deficiency of CO_2, representing the deoxidation of the $Fe_2 O_3$, leads one to suppose that the ore gets very speedily broken up, probably by the facility with which it absorbs carbon,* and, in a half-reduced state, runs down through the coke, and, arriving in a highly-heated region, a loss of fuel ensues by the action of CO_2 on the C. If, however, it is mixed with large blocks of Cleveland stone, this rapid descent may possibly be prevented, and the operation effected without this waste of heat.

Granting the merit due to Mr. Whitwell of having succeeded, by the Consett mode of treatment, in doing that which has not been done in respect to coke consumption by the smelters of pure hæmatite themselves, I still am unshaken in the belief that, having regard to the richness of the burden used at Consett, the consumption of fuel was no less than it ought to be, were it treated in furnaces 80 feet high with air less highly heated, as indeed was proved by experience at the Eston Works, mentioned in Section XXXI.

Mr. Whitwell, in No. 3 of his conclusions, endeavours to show the fallacy of my former arguments by stating that, as the blast is lowered 200°F., there is an increase of 2 cwts. in the consumption of coke.

There is an obvious error in this statement, unless it could be shown that, along with this increment in the temperature of the blast, there was also a larger generation of CO_2 in the upper part of the furnace, whereas the analyses of the Consett gases prove the reverse to have happened.

	Exp. 807. No. 4 Furnace.	Exp. 808. No. 4 Furnace.
Temperature of blast ...	1,107°F.	1,324°F.
Composition escaping gases—		
CO_2	14·2	11·7
CO	31·2	29·17
H	1·3	...
N	53·3	59·13
	100·	100·
100 vols. CO = Vols CO_2 ...	45·5	40·2

* *Vide* Exp. 213. Lanch. Hæmatite—100 Fe absorbed 65·3 C in 7½ hours at 415° C.
Do. do. 214. Do. do. 100 Fe absorbed 531· C in 7½ hours at 415° C.
Do. do. 215. Cleve. calcd. stone—100 Fe absorbed 4·68 C in 7½ hours at 415° C.

Omitting the loss of heat from the deficiency of CO_2, it is easy to compare the heat evolved from 2 cwts. of coke with that represented by 200°F. in the blast.

The weight of air, using 19 cwts. of coke per ton of iron, will be about 90 cwts., which, for every 200°F. (111°C.), contains (90 cwts. × 111°C. × ·237 Sp H) 2,367 calories. Now, 2 cwts. of coke burnt to CO with blast at, say, only 600°C., is as follows:—

Air to burn 2 cwts. (Coke.) 11·5 cwts. × 600°C. × ·237 Sp H = 1,635 calories.
„ 2 cwts. = 1·9 carbon × 2,400 = 4,560 „
Together ... ... 6,195 „

It is, therefore, highly improbable that the substitution of 2,367 calories, contributed by the blast, would permit the suppression of 6,195, afforded by the coke. I do not, of course, for one moment doubt, that so candid a writer as Mr. Whitwell can produce many weeks' workings which will support his own views; but they will be found to arise from some of those exceptional circumstances, of which he makes mention in his paper, and which, probably, might be explained by a reference to the "composition of the gases," to which, in my opinion, he attaches too little importance.

It seems to me, however, that the figures, quoted by Mr. Whitwell himself, by no means present that invariable coincidence between the quantity of coke consumed and the temperature of the blast, as to justify the conclusion he so unflinchingly maintains.

Instead of following the periods quoted in a table, given in the paper, in their chronological order, I have arranged them according to their temperature, beginning at the highest, and attached to each is the coke used per ton of metal. It will be perceived that no such uniform correspondence, as he supposes, is found to exist.

Period.	Temp. F.	Coke. Cwts. q. lbs.	Average weeks' make.	Average number.
April 10, 1869, to Aug. 27, 1870	1,400	18 0 8	388	4·47
Feb. 25 ... „ Mar. 11, 1871	1,239	19 3 23	471	4·36
Mar. 11 ... „ Apr. 8, 1871	1,225	19 1 17	500	4·14
Aug. 27 ... „ Nov. 19, 1870	1,200	18 1 19	466	4·43
Nov. 19, 1870, „ Feb. 11, 1871	1,190	20 0 17	460	4·41
April 8 ... „ May 6, 1871	1,175	19 1 15	508	4·09
May 6 ... „ June 6, 1871	1,149	19 1 4	542	not given.
Feb. 11 ... „ Feb. 25, 1871	1,148	20 0 2	467	4·43

I would only point out here, that, with the blast given at 1,175

and 1,149°F., the coke used is 19.1.15 and 19.1.4, respectively, against 19.1.17, with the blast at 1,225°F.

I may add, I have gone carefully over 45 consecutive weeks' workings of this furnace, and classified the temperatures in the same manner as that followed above, and a still greater amount of variation is apparent. To avoid any unfair inference being drawn, I have arranged them in four divisions, so as to obtain a mean consumption of coke over as many average temperatures.

Consumption of coke at Consett, No. 4 Furnace, part 1870 *and part* 1871.

Temperatures under 1,150°F. 15 *weeks:*—

Temp.	Coke. Cwts.	qrs.	lbs.	Iron. Tons.
1061	22	0	14	460
1098	18	0	21	484
1106	22	3	12	455
1112	18	2	26	465
1122	17	2	17	477
1126	19	0	3	513
1132	19	1	20	532
1133	20	2	15	437
1133	19	2	26	452
1134	17	0	18	467
1140	20	1	6	447
1144	19	0	19	435
1145	19	2	9	488
1148	19	2	13	491
1149	19	1	18	483

Average—

Temp. F.	Coke. Cwts. q. lbs	Iron. Tons.	Yield ore per cent.
1125	19 2 8	472	45·63

Temperatures between 1,150 *and* 1,200°F. 16 *weeks:*—

1152	18	3	4	537
1158	19	1	25	476
1170	19	1	19	543
1172	18	3	20	539
1173	19	0	1	483
1174	19	3	23	455
1176	19	2	10	507
1177	19	3	22	415
1178	19	0	19	476
1181	19	1	27	462
1183	22	3	7	201
1183	19	3	24	491
1184	20	2	1	455
1184	19	1	1	456
1194	19	1	26	495
1199	19	1	9	503

Average—

Temp. F.	Coke. Cwts. q. lbs.	Iron. Tons.	Yield ore per cent.
1177	19 2 4	468	46·27

Temperatures between 1,200 *and* 1,250°F. 12 *weeks*:—

Temp.	Coke. Cwts.	qrs.	lbs.	Iron. Tons.
1201	18	1	24	506
1201	19	0	13	577
1208	20	2	23	465
1208	19	0	21	470
1208	18	3	14	462
1219	19	0	22	510
1230	19	0	26	511
1236	18	3	3	470
1236	20	2	1	478
1236	19	0	19	478
1243	19	3	19	482
1245	20	1	19	468

Average—

Temp. F.	Coke. Cwts.	q.	lbs.	Iron. Tons.	Yield ore per cent.
1221	19	2	4	491	46·41

Temperatures 1,250°F., *and above.* 4 *weeks*:—

1260	19	1	18	484
1283	20	0	20	508
1292	17	2	8	431
1316	19	2	4	504

Average—

Temp. F.	Coke. Cwts.	q.	lbs.	Iron. Tons.	Yield ore per cent.
1288	19	0	19	457	45·49

For a furnace of the size of this, 55 feet high, the make is remarkably good, but an inspection of the figures will fail to connect it with the highest ranges of temperature, and still less is the alleged saving of 2 cwts. of coke for every 200°F. of temperature in the blast perceptible. My own impression is that, if the furnace had been blown throughout at 1,100°F. to 1,150°F., probably just as good results would have been obtained as those got by heating the air to 1,300°F., but of this any one can judge for himself. The iron made was all forge, chiefly No. 4, the average being about 4·33, and to satisfy myself that the coke consumption account was not influenced by any differences in the richness of the minerals, each division, upon which the averages are calculated, contains a note of the yield reckoned upon the hæmatite and calcined Cleveland stone which was used. I shall, in the next section, have to direct attention to a somewhat remarkable case of economical use of combustible at Eisenerz in Styria, of which the particulars will be given at the proper time. At present, however, I may observe that in former years the blast at Eisenerz was only heated to 200°C. (392°F.) On receiving intimation of what had been accomplished in the vicinity of Middlesbrough, my friend, Prof. Tunner, recommended an increase in the temperature of the air, at the Styrian Works, which was

raised to 400°C. (752°F.) The weight of fuel used does not appear to have been materially affected by the change.

There has been going on, for some months past, a very important experiment at the Ormesby Works, near Middlesbrough, of which no doubt the iron trade will look for the details with great interest —I mean that connected with the huge furnace, 90 feet high, with boshes of 30 feet, and containing above 40,000 cubic feet. It receives its hot air from a range of magnificent fire-brick stoves, each 50 feet high, admirably arranged, and so powerful that upon one occasion I found the indicated temperature was 1,350 and 1,400°F. One cannot be surprised that so gigantic a piece of apparatus should have presented some difficulties on first starting it, and in consequence its designer, Mr. Charles Cochrane, is unable, he informs me, yet to speak positively as to its performance.

Since writing the preceding portion of this section, by the assistance of Mr. J. T. Smith, of the Barrow Works, very willingly rendered, I am placed in possession of facts bearing directly, and in a very conclusive manner, upon the oft-debated subject of the value of superheated air.

Some time ago, at this establishment, there was erected a new furnace, 75 feet high, with boshes of 19 feet, receiving its blast from a range of fire-brick stoves, erected from the designs of Mr. Cowper. When set to work, it proved so unmanageable in smelting the Lancashire hæmatite that it had to be stopped, and its height reduced to 61 feet. This alteration removed all difficulty, and the furnace now performs its duty with superheated blast with ease.*

After it was at regular work, Mr. Smith kindly undertook to register the temperature every half-hour for sixteen days. This varied from 1,075 to 1,125°F., with one exception, when it fell to 1,000 and rose to 1,150°F., during six hours. We may, therefore, take the average at 1,100°F. (593°C.)

In the sixteen days, the make was 1,189 tons, average No. 2·25

Coke consumed per ton of iron	...	Cwts.	20·08
Limestone ditto.	...	„	7·61

I estimate, instead of having about 29 cwts. of slag per ton of iron, there would only be about 11 cwts. in the case we are considering,

* This is the same furnace already alluded to in the present section.

and instead of the liberated CO_2 of the limestone carrying off 1·4 cwts. of carbon (by $CO_2 \times C = 2\ CO$) only ·91 cwts. would so escape. These two differences are equivalent to 3 to 4 cwts. of coke, *i.e.*, a furnace using Cleveland stone making a ton of No. 2·25 iron with 23·08 to 24·08 cwts., would be working as well as this furnace; hence, I infer that 108°C. (226°F.)* in this case has either been uselessly expended, or because the mechanical difficulties connected with the treatment of ore in a lofty furnace are such as to compel the use of a smaller one. To overcome this defect a high temperature of blast is required.

I do not possess the necessary data to form an exact estimate to show which of these two explanations is the correct one; but an approximate calculation may be made on the basis of the gases having the same temperature, and being as highly charged with O as those in the Middlesbrough district, using their usual quantity of coke.

Fuel consumed per ton of iron ...	20·08			
Less impurity 6 per cent. ...	1·20			
		18·88		
C in Limestone carrying off equal weight from fuel ($CO_2 \times C = 2\ CO$)		·91		
				Cwt. units.
		17·97	× 2,400	= 43,128
C of the CO burnt to CO_2, say		6·5	× 5,600	= 36,400
Heat in 95 cwts. of blast ($95 \times 593°C \times ·237$ Sp. H				= 13,342
				92,960

Now, if we take 93,000 cwt. heat units as the absorption (*vide* Section XXVII.) for making Cleveland iron, 80,000 to 82,000 should have been ample, after allowing for the lesser weight of slag and limestone, in producing hæmatite iron. Under these circumstances it seems pretty evident that, as in the Consett furnaces using superheated air, and in the Askham furnaces using air moderately heated, about 2 cwts. of C, which ought to

* The 108°C. is the difference between the temperature usually employed at the Clarence Works (485°) and that being used during the above exp. (593°).

have left the furnace as CO_2, have been reduced to the condition of CO.*

That which the incompleteness of the data in the above estimate leaves in doubt is, however, fully explained by the succeeding observations of Mr. Smith, at the furnace just described.

The actual heat required to make a ton of hæmatite iron is some 10,000 to 12,000 calories less than that capable of being evolved by 20·08 cwts. of coke, burnt with air at 593°C., provided 6·5 cwts. of C escaped as CO_2. Either this proportion of the oxidizing gas (CO_2) is incompatible with the reduction of Lancashire ore used at Barrow, or the temperature of the blast has reduced it to CO. The next experiment of Mr. Smith inclines me to the latter belief. In it, the blast was maintained steadily at 1,450°F. to 1,550°F., say an average of 1500°F. (815°C.), or 400°F. (222°C.) above that of the former trial.

Now this afforded a proper opportunity to test the accuracy of Mr. T. Whitwell's assertion, that 200°F. was equal to 2 cwts. of coke—for we have the furnace, with its blast already at 1,100°F., making iron with even an excess of coke, compared with the duty performed by a Cleveland furnace of 80 feet, fed with air at about 900°F. Surely the virtue of the 400°F. just added ought to have made itself felt in such a case as the present.

The reply shall be given in Mr. Smith's own words, contained in his letter of 16th December, 1871 :—

"I think we may consider the experiment has lasted long enough to prove that the excessive temperature (1450°F. to 1550°F.) had no effect whatever in reducing the coke, and the results of the eight days are as nearly as possible identical with the previous sixteen.† The make of the furnace has been 604 tons, the consumption of coke 610 tons, and of limestone 230 tons, and the ore has yielded 55 per cent. To look at the question in a more practical form, I may mention that during the 24 days the charge was never altered in any way, and when the high heat had commenced, there

---

* Amount of calories evolved by supposed combustion of 20·08 cwts. coke 92,960
Deduct 2 cwts. less C supposed to escape as CO instead of CO_2, 2 × 5,600 11,200

Leaving 81,760

† Blast at 1075°F. to 1125°F., average 1100°F.

was no difference whatever, either as to the cinder or qualities of iron."*

It would have been satisfactory to have been able to confirm the opinions just quoted, by the exact figures obtained from the performance of the Carlton furnaces, heated by means of stoves built under the superintendence of Mr. Whitwell himself. Mr. Ramsay, the director of this establishment, not having had an opportunity of extracting these, I can only quote from the general information which this gentleman has kindly given. The furnaces themselves are 85 feet high, with boshes of 18 feet, and are working with a stone which in its calcined state yields only 38 per cent. Making allowance for the difference of circumstances involved in these conditions, they have, in none of the frequent communications Mr. Ramsay has made to me, been performing better (less consumption of fuel) than works using precisely the same ore, and getting their blast at 485°C. (905°F.), although at Carlton the indicated temperature was 1,300°F. to 1,400°F. In addition to this, when a second furnace was receiving its air at 950°F., it was doing its work about as well as the other, at which the blast was heated to 1,350°F., and further, when this second furnace had its air raised to 1,200°F., little or no improvement was perceptible.

At another place in the neighbourhood of Middlesbrough, the same ironstone is treated as that used at the Carlton Works. In this case, the furnaces are blown with air heated in the ordinary cast iron stoves, and I have good authority for stating that the coke consumed at the one is within a mere fraction of that used at the other.

After explaining the laws which appear to me to regulate the action of the blast furnace, I have quoted many instances of actual workings in confirmation of the views which have been laid down. These have led me to express with some degree of confidence that it is useless to hope to smelt a ton of grey iron from the Cleveland stone yielding 41 per cent. of pig metal with anything notably under 20½ cwts. of coke.

Notwithstanding this, it is only right to state that there are heard of in the North of England occasional instances of the work

* 604 tons of iron for 610 tons coke = 20·18 cwts. per ton.
230 ,, limestone=7·60 ,, ,,

having been done with less even than 19 cwts., and as these were communicated to me by firms whose word is not to be questioned, I think it proper not to withhold facts merely because they may raise a doubt upon the correctness of my own assumptions.

When, however, those tests are applied, which, under the variety of conditions described in Section XXVIII., brought out such a coincidence of results, there is found considerable discrepancies attending the working of furnaces with, what I feel justified in designating as, abnormal quantities of fuel.

In illustration of this, I would dwell for a few instants upon one remarkable case of a low consumption rate of coke, which was given me as obtained in furnaces having a height of 85 feet, with 27 feet boshes. Here the iron, generally grey forge, was stated to have been made with 18·38 cwts. of coke, the average over two months being 18·71 cwts., the ore (Cleveland) yielding 41·7 per cent. of No. 4 iron, and the limestone per ton of metal being 10·9 cwts.

Exp. 809. Four trials of the blast made with the electric pyrometer gave—

861°, 921°, 834°, 879°F.=average 873°F. (467°C.)

Exp. 810. Twenty-four readings of the temperature of the escaping gases afforded a mean of 318°C. (605°F.)

These numbers indicate pretty strongly that if the furnace in question is doing better duty than its neighbour, it is not because there is anything extraordinary in the quantity of heat it is receiving with the blast, nor in the unusually efficient way in which the escaping gases are surrendering their sensible heat to the incoming materials.

The gases were sampled over a period of $1\frac{3}{4}$ hours, and although this was repeated, in both cases an excessive quantity of CO_2 was apparent. I am, however, disposed to regard both sets of analyses as accidental, because the carbon in this form of combination amounted to more than the usual equivalent. Overlooking this discrepancy, it will be seen in the following estimate that the heat evolved, including that from the excess of C as CO_2, indicates a considerable deficiency, denoting an error somewhere in the figures, which error is further confirmed by the want of agreement between the oxygen, as shown by the analysis, and that in the blast and minerals.

The analyses of seven specimens gave:—

	CO_2	CO	H	N
Exp. 811.	15·5	25·5	·9	58·1
	16·1	25·4	·9	57·6
	15·0	26·0	nil.	59·0
	15·1	26·8	nil.	58·1
	15·3	26·4	·1	58·2
	15·0	25·5	·8	58·7
	15·4	24·6	·9	59·1
100 vols. ...	= 15·34	25·74	·52	58·40
100 parts weight*	= 22·22	23·79	—	53·99
Carbon ...	= 6·06	10·19	—	— = 16·25
Oxygen ...	= 16·16	13·60	—	— = 29·76

Taking the coke at 18·75, and limestone at 10·9, we have, for heat development:—

		C in coke and lmest.
Coke used per ton of iron, 18·75 ; less 7½% imp. 1·4 = 17·35		18·66
C, in limestone, carrying off equal weight C ... 1·31		
	16·04 × 2,400 =	38,496
C of this CO burnt to CO_2 ...	6·73 × 5,600 =	37,688
		76,184

Gases, weight per ton of iron—

Total carbon, per ton of iron, in coke and limestone...			18·66
Less taken up by iron...			·60
Weight of carbon in gases			18·06
Nitrogen (16·25 : 53·99 : : 18·06 :) ...	60·00		
CO_2 ... (53·99 : 22·22 : : 60·00 :) ...	24·70 =	6·73C +	17·97 O
CO ... (53·99 : 23·79 : : 60·00 :) ...	26·44 =	11·33 „ +	15·11 „
Water and hydrogen	·56	—	—
	111·70	18·06 „	33·08 „

Weight of blast—Nitrogen as above...	60·	
Oxygen with do. ...	17·97	
Moisture	·50	
		78·42 cwts.

* The calculation is based on average composition of the two sets of analyses.

Comparison of oxygen—per ton of iron, as above, ...		33·08
Oxygen in blast	17·92	
„ in moisture of blast ...	·44	
Ore	9·00	
Limestone	3·49	
		30·85
Difference, showing error		2·23
Total heat statement—		
From oxidation of carbon, as before		76,184
Contributed by blast...78·42 × 467° × ·237 S.H.		... 8,676
		84,860
Less in gases ... 111·70 cwts. × 318° × ·24 S.H.		... 8,522
		76,338

There appear certain discrepancies in this estimate which I am unable to reconcile. There is too much oxygen, which indicates probably that too high a percentage of carbon has been reckoned as CO_2, which seems probable on the face of this statement. Assuming, however, that the quantity of CO_2 is correct, the number of heat units is considerably below that found upon previous occasions as being required to the ton of iron. Making allowance for the heat contained in the ironstone, the difference is not far from that represented by 2 cwt. of coke burnt to the state of CO.

Mr. B. Samuelson, M.P., has given, in a paper to the Institution of Civil Engineers,* a very comprehensive description of two furnaces he has recently erected at Newport, near Middlesbrough. In it, every particular is clearly set forth of what constitutes a smelting plant of the most modern and most efficient character, and, in justification of this praise I may add that I am not aware that any furnaces in their neighbourhood are doing better duty, and a good many, I believe, are not doing as well.

Mr. Samuelson mentions, as an exceptional result, their having made during one week a ton of iron with 18·78 cwts. of coke, but he also alludes to the calcined Cleveland stone having yielded 45·29 per cent., the average of this kind of stone, he states, being 37 to 40 per cent. Either there has been metal made, during the

* *Vide* "Minutes of Proceedings of Civil Engineers," 1871.

period in question, carried into the account belonging to previous workings, or the ironstone used has differed considerably from that character upon which my statement as to fuel consumption was based. In neither case, therefore, can the figures quoted in this paper be considered as impugning the correctness of the estimate I have formed of the *minimum* heat, and therefore the *minimum* fuel required in the process for smelting an ore affording 41 per cent. of metal.

The author, with that candour which marks the intercourse of the Cleveland ironmasters, and which I believe has greatly tended to the advancement of their common interests, gives many particulars of the work performed. The average quantity of ironstone consumed is given at 46·11 cwts. per ton of iron, equal to 43·37 per cent., which is above that usually obtained from Cleveland ironstone calcined. The average of the fuel was 20·35 cwts.

By permission, kindly granted by Mr. Samuelson, I have been allowed to examine the furnaces described in his paper.

Exp. 812. The blast, as determined by Siemens' electric pyrometer, had a temperature of 516°C. (961°F.), and the gases averaged over two hours, 305°C. (581°F.), but as this did not include the dinner hour, when it rises considerably, 320°C. (608°F.) would probably, therefore, be about the actual mean.

Exp. 813. The gases were sampled at seven different times, and contained, on the average—

$$CO_2\ 11{\cdot}7,\ CO\ 28{\cdot}3,\ H\ 1{\cdot}2,\ N\ 58{\cdot}8 = 100 \text{ vols.}$$

In this, the CO_2 is to the CO as 41·34 vols. to the 100, corresponding closely with what is the usual ratio.

Calculated upon the burden of mine carried upon a given weight of coke, and assuming it to yield 41 per cent., the consumption of fuel was 21·42 cwts. per ton of metal. Upon this occasion, the flux was used in its calcined state, so that, with raw limestone, the probable quantity of coke would have been 22 cwts.

These furnaces are 85 feet high, 28 feet across the boshes, and contain 30,000 cubic feet.* The temperature of the blast was very good, nearly 1,000°F., and, according to my opinion, their performance was excellent. Notwithstanding this, *quite as favourable results* are at this moment being obtained from one of the Clarence

* *Vide* "Gjers on Cleveland Blast Furnaces, Journal of Iron and Steel Institute, November, 1871, p. 207."

furnaces of 15,500 cubic feet, with its blast a few degrees below 900°F. If this is not conclusive evidence that the profitable limits of dimensions of furnace, and temperature of blast have been reached, and, indeed, exceeded, I do not know where we have to look for the proof. It is true, Mr. Samuelson himself states that in some other furnaces of his own, containing 16,000 cubic feet, the fuel was 15 per cent. above that of the larger ones just mentioned. This is equal to 24 to 25 cwts. per ton of iron; but inasmuch as they are only 69 feet high, instead of 80 feet like those at Clarence, it cannot from this be inferred that 16,000 cubic feet, contained in suitable dimensions, is not amply sufficient for the work, so that taking the facts as stated by Mr. Samuelson, I think I am entitled to say they confirm, to the letter, what has been advanced in these pages.

A few words, before concluding this section, in reference to the shape of the furnace, to which attention was called at the conference of the Institution of Civil Engineers, already alluded to.

No one can be more sensible than I am of the fatal effects which may arise from an improper manner of distributing the materials in charging. In the case of the first furnaces, over which I had control, which were open-topped, charged at one door, but this was subsequently altered so that the materials were delivered at four openings. This change produced a saving of 30 per cent. in the fuel, and an increase of above 50 per cent. in the make. The mere contraction of a couple of feet in the diameter of the throat threw a furnace, upon another occasion, from foundry to white iron, in which manner it continued to work so long as the narrowed throat was persevered in. As soon as this was abandoned, the iron became grey. The imperfect mode of distribution spoken of above may also be an accompaniment of improper shape of the furnace, or of faulty construction in the cup and cone. When the escaping gases were first utilized at the Clarence Works, a considerable derangement took place in the working of the furnaces, which was remedied by enlarging the cone, so as to spread the materials more evenly, and if the more recent observations at Consett, in respect to the larger furnace (No. 5) not being prejudicially affected by receiving its blast at too high a temperature are correct, then it must be concluded that its defective performance, when compared with No. 4 furnace at these works, is due to a want of suitability in its proportions.

I am by no means prepared to deny that up to a certain capacity, shape in a blast furnace may be very important, and I am, therefore, prepared to accept any properly authenticated statement, either that Alger's elliptical furnace or Rachette's oblong one may be very useful. It must, however, be borne in mind, that all the changes in form, just referred to as having beneficially affected the furnaces upon which they were made, were applied in instances when the duty performed was greatly below that attained in more recent times, in furnaces sufficiently large. If later improvements have enabled us to deprive the gases of as much of their sensible heat as is practicable, and at the same time to exhaust their reductive power, I for one must decline believing that either of these offices can be sensibly altered by a mere change in the shape of the vessel in which they are carried on.

SECTION XLIII.—ON THE SMELTING OF CERTAIN ORES BY MEANS OF CHARCOAL.

In the different calculations which have, hitherto, been made use of to determine various questions connected with the smelting process, the mineral treated was considered to be that of the Cleveland Hills.

Regarded as a mere question of heat absorption, I have endeavoured to show that perfection consisted in allowing the gases to escape as completely deprived of their sensible heat as the nature of circumstances permitted, and to be charged as fully with oxygen gas as is consistent with the character of the operation.

I have given, at some length, my reasons for believing that when the temperature of the gases was reduced to 330°C. (626°F.), or thereabouts, they were all but inert on calcined Cleveland ore, when to every 100 vols. of CO they contained from 40 to 45 vols of CO_2.

I have further given proof, by quoting from actual experience of the furnaces at the Clarence Works, that these two conditions

were achieved when a capacity of 12,000 or 15,000 cubic feet was reached, and when the air was heated from 480° to 500°C. (896° to 932°F.)

No doubt the reducing energy of the escaping gases may be augmented by an increase of temperature in the upper portion of the furnace, which, of course, could be effected by superheating the blast; but I have also endeavoured to demonstrate that, when this is done, a secondary action is set up, by which the CO_2 resulting from the process of reduction, aided by this additional temperature, dissolves C, and thus neutralizes the advantages derived from this means of increasing the fund of heat in the furnace. Quoting from the experience of smelters who operate upon the richer and differently constituted ores of Lancashire and Cumberland, which yield their oxygen with great rapidity to the reducing power of CO, it is needless to employ furnaces above 55 to 60 feet in height. I now propose to consider some cases where the dimensions are so small that the materials pass from the throat to the hearth of the furnace in little more than four hours, and in which the proportion of CO_2 to CO present in the gases is so large that it looks as if those laws which govern the smelting of iron from Cleveland and other ironstones of the argillaceous description, as well as the richer hæmatites of Lancashire and Cumberland, with coke, experience considerable modification where other material is reduced by means of charcoal.

If a drop of sulphuric acid is added to a solution of nitrate of barium a sulphate of this metal is precipitated, and it is usual to explain the action by stating that the affinity of sulphuric acid for barium is more powerful than that of nitric acid.

If a current of CO_2 is passed over carbon as it exists in soft coke at a given temperature, the CO_2 is decomposed and two equivalents of CO are formed. In this case, it may be said that the affinity of a molecule of C for its first equivalent of oxygen is stronger than that possessed by another carbon molecule, for the second equivalent of this gas. Other varieties of carbon, such as that in hard coke, under precisely similar circumstances, I have shown, remain unaffected, although the actual order of affinities, as between C and O, just mentioned, remains, of course, unchanged.

In like manner, when a mixture of CO and CO_2 is conducted over two varieties of Fe_2O_3 such as those described in Exps. 99 and

101, in which 100 vols. of the former and 50 vols. of the latter were brought in contact with calcined Cleveland stone, and Fe_2O_3 obtained by precipitation, the effect is very different, inasmuch as, at the same temperature and in the same time, the pure Fe_2O_3 lost four times as much of its oxygen as the iron oxide in the molecular form in which it exists in Cleveland ore.

This difference of behaviour, of course, cannot be set down to the reducing gas, CO, having a more powerful affinity for the oxygen in one form of the same substance (Fe_2O_3) than in another.

In comparing the treatment of the same kind of ore in furnaces of different capacities, the value of *time* in the conflict of opposing forces which are at work in a blast furnace, has been made sufficiently apparent. In such cases, the periods of time dealt with had a very appreciable duration, but it is probable, indeed certain, that where they do not admit of actual admeasurement, owing to the rapidity of the exchange of elements, it is *time*, all the same, we must look to for an explanation of phenomena which appear, at first sight, contradictory in their nature.

If, for example, at a given depth in a blast furnace, where a certain temperature prevails, no CO_2 is to be found, and in another, using a different ore but other circumstances being equal, a considerable quantity of this acid is always present, without interfering with the process of reduction, it may be inferred, in the first case, that the rapidity of CO_2 to part with O to C is greater than that with which CO absorbs O from the ore; and, in the latter, the reverse of this action is what happens.

This reversed action may also take place with the same ore, but, when the forms of carbon are different, as we have seen, according to whether the coke is hard or soft. When hard, the action of CO_2 on it is so slow, that deoxidation of the ore is much more rapid than the action $CO_2 + C = 2\ CO$. On the other hand, when the coke is soft, the carbonic acid dissolves C so rapidly that the quantity arriving at the hearth for combustion, is so much diminished as to augment very notably the consumption of fuel.

The preceding remarks are suggested by the analyses contained in a paper,* by Professor Tunner, previously referred to, which contains the following facts.

* Theorie des Hauts Fourneaux. Revue Universelle, 1860, 1. Sem. p. 464.

Composition of gases of the Wrbna blast furnace, working with calcined Eisenerz ore (spathose, or brown hæmatite) and charcoal:

Distance from throat.	By volume. N	CO_2	CO	By weight. N	CO_2	CO
About 10 ft. 9 in.	70·50	16·39	13·11	63·50	23·56	12·94
„ 17 6	71·36	17·80	10·89	60·52	24·86	14·62
„ 22 6	68·81	9·60	21·59	64·90	14·26	20·84
„ 27 8	66·66	2·68	30·66	65·65	4·15	23·20
„ 34 6	66·34	11·60	22·06	62·25	17·07	20·70

Volumetrically, the CO_2 to 100 vols. of CO is as follows:

	CO_2 By weight.	Temperature.
At depth of 10 ft. 9 in.	125 vols. 182	558°C
„ 17 6	163 „ 170	Between 580 and 840
„ 22 6	44 „ 68 „	840 „ 910
„ 27 8	8 „ 18	950
„ 34 6	52 „ 82	1450

The Wrbna furnace is 36 feet high, with a capacity of only 1,200 cubic feet, and makes, notwithstanding, 140 tons of iron per week, it therefore presents interesting matter of enquiry, particularly, when it is remembered, 14 cwts. of charcoal, per ton of iron, burnt with air at 200°C. (392F.) was the quantity of fuel consumed.

Wishing, in the first instance, to be assured that the analyses given above really represented an average of the composition of the gases, I suggested to Professor Tunner the desirability of making a second series. This was kindly done by my excellent friend, but, upon this occasion, the blast had been raised to 400°C. (752°F.) The specimens were collected by means of enamelled pipes, so as to avoid any action by passing over metallic iron, the material formerly used for obtaining the gas. The charcoal now was reduced to 13·20 cwts. per ton of metal.

Composition of gases at Wrbna furnace, 1871, by weight:—

	N	H, &c.	CO_2	CO		100 CO = CO_2
Escaping gases	54·46	·67	21·47	23·40	=100	92
„ 2nd trial	54·90	·39	20·90	23·81	=100	88
18 feet from throat	53·38	1·01	19·79	25·82	=100	76
25½ „ „	54·57	·27	20·29	24·87	=100	81
28 „ „	55·00	·24	18·50	26·26	=100	70
32 „ „	54·34	·20	18·14	27·32	=100	66
34 „ 6 in. „	57·35	·11	4·61	37·93	=100	12

It will be observed there is a considerable variation between the figures contained in the first and the repeated series of analyses, but whether this is due to the difference in the temperature of the blast, or to some of those irregularities already spoken of, I am unable to say. One thing, however, is certain, viz., that there is in both sets an excessive amount of CO_2 in relation to the CO when compared with the gases emitted in smelting Cleveland stone.

Now, the explanation I would give of this large quantity being present is, that when the reducing agent CO is rushing through the furnace it takes up O and passes into the condition of CO_2 more rapidly than the resulting CO_2 takes up C, and it is the amount of the difference between these two reactions that constitutes the difference between smelting the calcined ore of Eisenerz with charcoal, and that of Cleveland smelted with coke.

The difference in question may arise from one of two causes, either charcoal must be much less easily attacked by CO_2 than coke, or the Eisenerz ore is much more susceptible of reduction than that of Cleveland, or it may be a combination of both these differences that constitutes the change of condition. Experiments were undertaken to determine which of these two causes produced the remarkable deviation in question.

The soft and porous nature of charcoal rendered it extremely unlikely that CO_2 could act less energetically on it than on hard coke. This, however, was subject for experiment, and not opinion.

Exp. 814. 18 grains of well burnt silvery coke were placed in a combustion tube, heated to a good red, in a Hofman's double gas furnace, and 800 c.c. of dried CO_2 were passed over it in 30 minutes.

The resulting gas consisted of—

CO_2	... ...	94·56 vols.
CO	... ...	5·44 „
		—— 100 vols.

showing the action was very slight.

Exp. 815. Made to compare the action of soft coke on CO_2 with that of hard coke and that of charcoal. Alongside of the tube used in previous experiment, a similar quantity of a very open and soft specimen of the coke was exposed under similar circumstances as to temperature, time, and quantity of CO_2 passed over it.

The issuing gas was composed of—

CO_2	69·81
CO	30·19
	—— 100 vols.

In this case the action was very rapid, nearly one-third of the resulting gases being CO.

To satisfy myself that this more rapid decomposition was not due to a large quantity of H being present in the coke, the two specimens were analyzed—the sulphur being disregarded.

	Exp. 816. Hard Coke.	Exp. 817. Soft Coke.
Carbon	93·49	84·83
Hydrogen... ...	·37	·92
Oxygen, difference	nil.	1·47
Ash	6·67	12·78
	100·53	100·00

Exp. 818. The tube was now filled with charcoal, in pieces as nearly as possible the same size as the coke, and dry CO_2 passed over it at the same rate as in Exps. 814 and 815. Owing to the lightness of the charcoal it only weighed 6 grains. 800 c.c. of the CO_2 passed over in 30 minutes at a good red heat.

Issuing gas contained—

CO_2	35·2
CO	64·8
	—— 100 vols.

Exp. 819. A second experiment, with a somewhat quicker current of CO_2, gave—

CO_2	57·14
CO	42·86
	—— 100 vols.

These experiments prove incontestably that the advantage manifested in smelting the Eisenerz ore is not in any way due to any superior power charcoal possesses in resisting the action of CO_2.

The next stage was to examine and compare the readiness with which the ores used in this Austrian furnace yielded their oxygen when exposed to the reducing gas. They consisted of spathose ore

as Fe CO_3, and of the same bed of mineral in various states of alteration, caused by atmospheric influence. They were designated:—

No. 1. Spathose unaltered ore.
„ 2. Spathose ore slightly oxidized, first stage.
„ 3. „ changed into "Braunerz" (br. hæmatite).
„ 4. „ „ "Brauner Glaskopf."
„ 5. „ „ "Plauerz."

Specimens of these, calcined, and of thoroughly roasted Cleveland stone were exposed simultaneously in the lead bath arrangement, with the usual precautions, to a current of CO for 8 hours at a temperature of about 400°C. (752°F.)—zinc barely softened.

	Exp. 820. No. 1.	Exp. 821. No. 2.	Exp. 822. No. 3.	Exp. 823. No. 4.	Exp. 824. No. 5.	Exp. 825. Cleve.
Original O removed %	77·73	91·31	29·5	42·92	17·18	41·91
C deposited per 100 Fe	1·00	2·10	7·41	18·01	4·71	2·32

The above experiments were repeated—

	Exp. 826. No. 1.	Exp. 827. No. 2.	Exp. 828. No. 3.	Exp. 829. No. 4.	Exp. 830. No. 5.	Exp. 831. Cleve.
Original O removed	65·3	74·1	30·3	40·8	17·	39·3
C deposited per 100 Fe	1·55	2·0	7·2	18·5	4·7	2·8

The next series were tried also during 8 hours, at same temperature, to oxalic acid gas (equal vols. CO and CO_2).

	Exp. 832. No. 1.	Exp. 833. No. 2.	Exp. 834. No. 3.	Exp. 835. No. 4.	Exp. 836. No. 5.	Exp. 837. Cleve.
Original O removed %	29·2	31·2	12·89	9.71	6·48	9·35
Carbon deposited	nil.	nil.	nil.	nil.	nil.	nil.

In every case it will be seen that Nos. 1 and 2, which, I believe, from the chief bulk of the ore smelted, lost oxygen very much more rapidly than Cleveland stone, and when this loss of O was not greater, or was less in the case of the altered ore than in Cleveland stone, the carbon deposition was much larger in the Austrian ore.

The circumstance, however, which bears more directly upon the greater ease with which the Eisenerz ore is smelted is the great difference which exists when the CO_2 has greatly weakened the reducing power of the CO. Thus, while Nos. 1 and 2 of the

spathose ore have lost something like half the oxygen in oxalic acid gas (equal vols. CO and CO_2) which they did in pure CO, the Cleveland stone, under the same circumstances, has had its loss of oxygen reduced to one-fourth.

In order to compare the behaviour of calcined Cleveland stone with calcined spathose ore, under circumstances more analogous to those which obtain in the blast furnace, the former was mixed with pounded coke, and the latter with pounded charcoal. The two mixtures were placed in separate combustion tubes, and heated simultaneously to a good red heat in the double Hofman's gas furnace, during which a stream of oxalic acid gas was passed over them.

Exp. 838. Of calcined Austrian spathose ore, containing 58·4 per cent. of Fe, 20 grains were mixed with 7 of charcoal. Passed over it 8 litres of a mixture of CO and CO_2. Time of experiment, 45 minutes.

Loss in weight of charcoal	...	1·679 grains.
„ of oxygen by ore		1·541 „
The charcoal has lost 23·9 % of its carbon.		
„ ore „ 31· % „ original oxygen.		

Exp. 839. 20 grns. of calcined Cleveland stone were mixed with 8 grns. of powdered hard coke, and the same quantity of oxalic acid gas was passed over it, as in Exp. 838, also during 45 minutes.

Loss of weight of coke ...	...	·358 grains.
„ „ O by ore	...	·611 „
The coke lost of its carbon	...	4·9 %
„ ore „ original O	...	17·4 „

These two experiments may be taken as confirming what has already been advanced respecting the relative action of CO_2 on charcoal and on coke, and the greater readiness with which the Austrian ore, compared with that of Cleveland, loses its oxygen.

In these two experiments, the gas used was obtained from oxalic acid, but, as it was stored over water, a portion of the CO_2 was absorbed, reducing it to a mixture of about 60 vols. CO to 40 CO_2. These experiments were repeated, and the composition of the current of gas ascertained before and after it passed over the mixtures of ore with coke and charcoal.

Exp. 840. 20 grains calcined Austrian spathose ore, mixed with 7 grains of powdered charcoal, exposed for 45 minutes, at a bright red heat, to a current of 64 vols. CO and 36 CO_2. About 3 litres of the mixed gases were passed over in the time.

The charcoal lost ... 1·540 grains equal to 22 per cent. of its C
„ ore „ ... 2·316 „ „ 46·2 per cent. original O

Three trials of the issuing gas gave the following results :—

	CO		CO_2	
100 vols. =	35·7	...	64·3	taken 10 minutes after commencing
„ „	70·7	...	29·3	„ 30 „ „ „
„ „	73·	...	27·	„ 50 „ „ „

Exp. 841. 20 grains calcined Cleveland ore, mixed with 8 grains powdered hard coke, were treated in a similar manner to that described in the last experiment, with the exception that the gas contained 60 vols. CO and 40 CO_2.

The coke lost ·405 grains, equal to 5· % of its C.
„ ore „ ·781 „ „ 22·3 „ original O.

The issuing gases were composed of—

	CO		CO_2	
100 vols. = ...	36·	...	64·	taken 10 min. after commencing.
„ „ ...	56·7	...	43·3	„ 30 „ „
„ „ ...	55·	...	45·	„ 50 „ „

As regards the issuing gases, in both cases the first trial may be disregarded from the apparatus not being fully heated. These being eliminated, we have 100 vols. of the issuing gases containing as follows:—

From spathose ore and charcoal 71·8 vols. CO ... 28·2 vols. CO_2
„ calcd. Cleveland and coke 55·8 „ CO ... 44·2 „ CO_2

We have, therefore, it will be seen, firstly, the Austrian ore losing its O much more readily than the English; secondly, doing so to a much greater extent in an atmosphere richer in CO_2 (*vide* Exps. 833 and 837); and thirdly, the gases have their reducing power constantly reinforced by the ready manner in which the charcoal absorbs O from the CO_2, producing fresh supplies of CO, which is ready to perform the office of deoxidation on fresh quantities of ore.

The furnace of Eisenerz contains only about 1,200 cubic feet, or

40 cubic metres, and, taking its make at 140 tons per week, and using 14 cwts. of charcoal per ton (no limestone being needed), its gases per ton will be about 67 cwts., or 2,600 cubic metres. Thus, per minute, there will rush up (at 760 m.m. and 0 c.) about 30 cubic metres of gases for 1,000 cubic feet of furnace capacity, which is (Section VI.) near three times that rising through one of the larger Cleveland furnaces.

In like manner the current of solid materials passing through each 1,000 cubic feet of furnace space per minute is ·62 cwts., which is four times the speed of that common in the vicinity of Middlesbrough.

The manner, then, in which I would account for the marked difference between the composition of the gases in a furnace smelting Cleveland ore and Austrian spathose, the former using coke and the latter charcoal, is as follows:—The stream of CO flowing up the Eisenerz furnace encounters the ore it has to deoxidize, as well as C, ready to reduce the CO_2 generated by reduction, back again to CO. The readiness, however, with which the oxygen is given up by the ore exceeds that with which the carbon of the charcoal is oxidized at the expense of the CO_2. In the coke furnace, the fuel, it is true, is much less easily acted upon by CO_2 than is the case with charcoal, but on the other hand, the Cleveland stone is so much more difficult of reduction as to produce a state of equilibrium in which the relation of CO_2 to CO is much less than that which obtains in the charcoal furnace under examination.

It may possibly be suspected that the cause of charcoal being able to perform its duty so efficiently in the Eisenerz furnace, *i.e.*, with so small a quantity, is due to its greater calorific power. This, however, is not so to any extent, for the calories evolved by the combustion of one of charcoal is, according to Andrews, 7,900, and according to Favre and Silberman, 8,080. In my estimates I have taken carbon as it exists in coke at 8,000, the mean of the value assigned to it by the same authorities, which gives about 7,600 for the coke itself.

I have endeavoured to prove that charcoal possesses no superiority over coke, in a heat-producing point of view, by the usual plan pursued in estimating the heat absorbed in producing a ton of crude iron. The following figures contain the particulars of an estimate of heat development in the Wrbna furnace, according to the analysis last given :—

CO_2	21·18	=	C 5·77	+	O 15·41	
CO	23·60	=	C 10·12	+	O 13·48	
H &c.	·53		—		—	
N	54·69		—		—	
Weight ...	100·00		15·89		28·89	

Carbon in gases per ton of iron—

Charcoal used, 13·2 cwts. less 15· per cent. imp.=C ...		11·22
No limestone used		—
		11·22
Less C dissolved in iron		·60
		10·62

Weight of gases per ton of iron—

			Carbon.	Oxygen.
Nitrogen ...	(15·89 : 54·69 : : 10·62) ...	36·55		
Carb. acid ...	(54·69 : 21·18 : : 36·55) ...	14·15	= 3·86 ...	10·29
Carb. oxide	(54·69 : 23·60 : : 36·55) ...	15·77	= 6·76 ...	9·01
Hydrogen, &c.		·35	10·62 ...	19·30
		66·82		

Comparison of O per ton of iron with that due from various sources:—

Brought in with 36·55 N of blast ...	...	10·92
„ moisture in blast, say ...		·30
„ ironstone*		8·14 ... 19·36
Difference, experimental error ...		0·6

Heat development...3·86 cwts. C to CO_2 × 8,000 = 30,880 calories.
„ ...9·34 „ C to CO × 2,400 = 22,416 „

Total cwts. charcoal 13·20 „	53,296 „
Heat in blast ... 47·8 cwts. × 400°C. × ·237 sp. heat	4,531 „
Total cwt. calories per ton of iron ...	57,827 „

Now, according to the data formerly used (Section XXVIII.) in calculating the heat absorption which takes place during the

* In Cleveland stone, this was taken at 9 cwts. due to P_2O_5, SO_3, &c. decomposed.

production of a ton of iron, it may be assumed that the purer metal of Eisenerz requires, in round numbers, for—

Evaporation of water in fuel		300
Reduction and carbon impregnation ...		34,600
Decomposition of H_2O in blast		1,500
„ of SiO_2, &c.		1,000
Fusion of iron		6,600
„ 12 cwts. slag		6,600
Transmission through walls		2,000
Tuyere water		1,000
Leaving for sensible heat in gases ...		4,227
		57,827

The fact that in the case under examination there is no $CaCO_3$ to decompose, less SiO_2 and other impurities reduced, and a much smaller weight of slag to meet, renders, of course, a small quantity of heat necessary than is required in smelting Cleveland iron. This is further diminished by the large make in a furnace of such inconsiderable dimensions as that at Eisenerz. The table of absorption contains numbers of a somewhat arbitrary nature, but I believe they are not wide of the truth, and so far it is satisfactory that they confirm the general conclusions of an estimate based on so small a consumption of fuel as 13·2 cwts., for under no circumstances is it likely that any error could exceed that represented by another cwt. of charcoal. At the same time, it must be remarked that it is not the unusually low quantity of fuel which is the especial subject of comment at the present moment, but the large proportion of CO_2, in which the ore, under consideration, is reduced. The small consumption of combustible is due, in a great measure, to the very small quantity of slag formed, fully a ton less than that which accompanies the smelting of Cleveland stone, and the absence of limestone as a flux. The difference in the quantity of fuel, from these two causes, will probably not be short of 6 cwt. to the ton of iron, so that the production of a ton of Cleveland metal, of low forge quality, with 19·20 cwts. of coke, would be about the same as a ton of a similar description of iron, made at Eisenerz, with 13·20 cwts. of charcoal.

It will be perceived that the peculiar property of the fuel, charcoal, is apparent in the analysis of the gases, because, although the deoxidation of the ore is so rapid that it outruns the oxidation

of C by CO_2, this latter action, nevertheless, goes on to a very considerable extent, as is evidenced by the fact that, whereas 6·58 cwts. of C should appear as CO_2 in the gases, per ton of iron, as due to the deoxidation and carbon impregnation of Fe_2O_3 by CO, 3·86 cwts. only are to be found in this form of combination.

I may observe, that it is possible, when the ore passes so rapidly down to the lower, and more highly heated part of the furnace, either by the charcoal itself, or by means of deposited carbon, reduction may take place under circumstances in which CO, and not CO_2 are the products of the action.

When it is considered that the fuel employed in the vicinity of the Tees is so much less easily attacked by CO_2, it might be supposed that more rapid driving of the furnaces might possibly be attended with a saving of fuel, by means of which CO_2, being formed lower down the furnace, the heat from its generation would, from having to pass through a higher column of the contents of the furnace, be more easily intercepted. The slowness, however, with which the Cleveland stone parts with its O probably prevents this, and, as a matter of actual practice, we have seen in the 6,000 feet furnaces, when the solids descend and the gases ascend more quickly than in furnaces double their size, the consumption of fuel is fully 25 per cent. above what it is in those of the larger capacity.

In the manufacture of forge iron in these Styrian and Carinthian furnaces, the consumption of charcoal, until the subject is properly examined, may seem unaccountably low. Thus, from returns I possess, extending over some months, I gather the following particulars:—

Work.	Cubic Feet.	Temp. Blast.	Weekly Make.	Charcoal ℔ Ton. cwts.
Lölling, 3 furnaces	...1,379	150°C.(302°F.)	111 tons No. 4.	13·43
Freibach, 1 „	...1,329	120°C.(248°F.)	140 „	12·14
Heft, 1 „	...1,580	170°C.(338°F.)	132 mottled	15·54
Eberstein, 1 „	...1,379	100°C.(212°F.)	97 „	15·58

I may add, however, that in other parts of the Austrian empire, I have had 21 cwts. of charcoal given me as being consumed for white iron, and as much as 31 cwts. for Bessemer, using an ore yielding 47 per cent., but in these latter cases 5 to 6 cwts. of limestone was used, whereas at the works already mentioned scarcely any flux was needed.

In connection with the greater or less consumption of combustible, German writers on iron smelting make use of the term "strengflüssig" and "leichtflüssig." If these words have to be taken in their literal sense of comparative susceptibility to fusion, their use, in my opinion, may lead to error. There are, no doubt, some differences in the melting points of different kinds of iron and slag, but these, I apprehend, are trifling and cannot account for the marked alterations, just spoken of, in the quantity of fuel required for mere liquefaction. The actual cause of the lesser quantity of consumption of combustible in small furnaces, I have conceived and described as being due to difference in susceptibility of reduction, and not of fusion.

SECTION XLIV.—SUPPLEMENTARY REMARKS ON CARBON IMPREGNATION BY DISSOCIATION OF CARBONIC OXIDE.

In Sections XI., XII., and XIII., the dissociation of carbonic oxide in its pure form, also when mixed with carbonic acid, and as it occurs in the blast furnace, was fully described. The two following sections contained enquiries into the changes experienced by metallic iron, and by an iron oxide, which have served to split up the CO, as well as an investigation into the nature of the alteration experienced by the carbonic oxide itself.

As regards the gas, there was no doubt, in addition to the precipitated carbon, a formation of CO_2, but it was also proved that in the case of metallic iron being used, there was a slight oxidation of the metal. It was considered that Fe itself was capable of dissociating the carbon oxide, and that when Fe_2O_3 was employed, there resulted, provided the action had been continued long enough, a mixture of

Metallic iron,
Unknown oxide of iron (Fe_x O_y), and
Carbon.

Thus while, according to the experiments detailed in the above-mentioned sections, metallic iron was capable of effecting the separation of carbon from carbonic oxide, it did not appear that the

presence of Fe, in its metallic condition, was absolutely indispensable for the dissociation of CO.

The delicacy of the experiment required to prove this was sufficiently explained when describing the modes of research employed. I do not think that the correctness of my conclusions, or the reverse, on the precise nature of the changes in question affect any of the arguments made use of in following the progress of the smelting process itself. In a scientific point of view, however, they are full of interest, and I am therefore well satisfied that my distinguished friends M.M. Grüner and St. Claire Deville, of Paris, have deemed the subject deserving of their attention.

The details of the investigations of these able chemists have not yet been published, but a private letter to myself, dated 20th Dec., 1871, from M. Grüner, contains some account of their labours. The following is a translation of what relates to the matter in question:—

"I have communicated to our Academy of Sciences an article on the reactions of CO on iron and on ores of iron, quoting you, of course, as the author of this interesting discovery. The article is a *resumé* of my experiments, performed during last year between the months of May and the end of November, and extracted from it are my conclusions, which appeared in the 'Comptes Rendus de l'Academie des Sciences de Paris.' The article itself will not be published until later, because the Academy has nominated a commission to report on my experiments, at the head of which is M. St. Claire Deville. This chemist has already verified the correctness of my conclusions, which I give below, observing, in the first place, that I do not agree with you on every point.

"1st, Carbonic oxide, *perfectly pure*, does not attack iron between 300° and 500°*; if there is a deposition of carbon, it is always caused by the presence of a small quantity of oxygen, either in the iron, or in the apparatus, or by the gas containing a little CO_2.

"2nd, On the other hand, as soon as the iron is slightly oxidized (and you know that perfectly deoxidized iron is scarcely to be obtained), or as soon as CO is mixed with traces of CO_2, or of O, carbon commences to be deposited by the action $2\,CO = C + CO_2$.

"3rd, But this decomposition of CO is never spontaneous; the

* It is presumed centigrade degrees are meant.

carbon which is deposited contains always *iron* and magnetic oxide. The carbon deposited, either on iron, by the mixture of CO and a little CO_2, or on the ore, by a prolonged action of CO, is *wholly attracted by a magnetised bar;* it is not pure carbon, but a ferruginous carbon containing 6 or 7 per cent. of iron.

"4th, It is equally certain that the deposition of this ferruginous carbon does not commence until the iron is *partially reduced to the metallic state.* No doubt, in operating on *pieces* of ore, the interior may remain intact; but outside of this there is a metallic pellicle, and carbon is deposited as soon as there is a faint pellicle of iron on the surface of the pieces.

"5th, The ferruginous carbon contains, *at the same time,* some metallic iron and some magnetic oxide, which is reproduced continuously in presence of oxygen or of CO_2. I account for the phenomenon by supposing that the ordinary oxide once reduced to the state of protoxide and suboxide—

we have $3\,FeO + CO = Fe^3O^4 + C.$,

and then $Fe_3O_4 + CO = 3\,FeO + CO_2$

and so on indefinitely, *provided there is a little* CO_2 *mixed with the* CO; without this, in time the FeO is completely reduced, and no more Fe_3O_4 appears. Carbon deposition then is arrested.

"We may equally have in the case of a suboxide—

$$3\,Fe^3O + 5\,CO = 2\,(Fe^3O^4) + 5\,C.$$

(the 5 C being combined with a little iron)

and then $2\,Fe^3O^4 + 5\,CO = 3\,Fe^3O + 5\,CO^2$.

As the suboxide, however, is hypothetical, the first reaction appears to me the more likely of the two.

"6th, Lastly, as regards the blast furnace, I am scarcely prepared to admit that the carbon thus precipitated is that which is found in the pig iron. As soon as the mixture of ore partially reduced arrives in an incandescent portion of the furnace, the carbon is burnt by the oxygen still remaining in the ore.

"In other respects, I entirely agree with your views on this decomposition of CO.

"I think, also, with you, that furnaces may be built needlessly high. It is evident that, beyond a certain height, the gases are not further cooled on account of the heat *developed* by the reduction of 2 CO into $C + CO_2$."

I do not feel myself warranted in calling in question statements,

of a purely scientific nature, made under such high authority as that of the names quoted above. In respect to the action of CO on calcined Cleveland stone, I would, however, remark, in connection with the fourth of the above-mentioned conclusions, that, so far from the surface of the ore exhibiting to the eye any trace of a faint pellicle of metallic iron, when the interior was blackened by the exposure to the gas of a blast furnace, there was generally, on breaking the mass, a thin covering of apparently red Fe_2O_3 found coating the exterior. I have imagined this might be due to an accumulation of CO_2, produced by the dissociation of the CO exercising an oxidizing influence on the outside of the fragments of ironstone.

To No. 6 of the conclusions, relating to deposited carbon being the source of this element in pig iron, I am also unable to state positively that my surmise on this head contains the true explanation of its origin. I am, however, not prepared to admit the soundness of M. Grüner's argument, which consists in supposing that all the deposited carbon, in ore partially reduced, must, or can be burnt by the oxygen remaining in the ore.

Now, if all the O, combined with 100 parts of iron, had to be removed by C as CO, which form of action would require the largest quantity of carbon, about 32 parts of this element would suffice for the operation. But I have shown in Exps. 278, 279, 280, and 281, that a current of CO removed 43·2—35·5—58·8, and 56·6 per cent. of the original O from Cleveland stone, and deposited per 100 of Fe, 125·6—195·3—358·5, and 140·6, respectively of carbon. It is clear, under such a state of things, the ore would be powerless, by means of the O it contains, to rid itself of such a superabundance of carbon.

If we turn to the furnace itself, we have this view entirely confirmed, *i.e.*, the deposited carbon is seen, as I have already upon more occasions than one pointed out, in enormous quantities.

If then, the assertion, that this form of carbon is the source of the element, is a mere inference on my part, I think it not an unreasonable one, viz., that iron, in the reduced ore, intimately impregnated with carbon, will more likely, at the moment of fusion, unite with a substance by which it is so thoroughly incorporated, than be melted first, and derive its C from the large fragments of coke over which it runs.

There is a fact in connection with the smelting of iron, which has, to myself, hitherto been somewhat difficult of explanation, and which confirms, I think, the opinion I have expressed on the existence of this large quantity of deposited carbon in the lower part of the blast furnace. If a fragment of fire-brick of the same quality as that which constitutes the hearth is so placed that a current of hot liquid slag flows over it, as soon as the brick acquires the temperature of the slag, or before, it is rapidly corroded, and speedily disappears. Now, what seems somewhat of a mystery, is the power of the masonry inside the furnace of withstanding, for several years, a current of nearly 100 tons a-day of this corroding slag.

I imagine this vast production of deposited carbon affords a solution to the mystery. In the lower part of the furnace it becomes, I think, incorporated into a kind of concrete, with slag, &c., and thus protects the actual surface of the brickwork from the action of the liquid contents.

It is well known to every furnace superintendent that the effect of a "scouring" cinder is to clear out all accumulation of slag, &c., from the hearth, and after this is done, the masonry itself is attacked. The colour of this scouring slag indicates the presence of a considerable quantity of unreduced oxide of iron, which, being brought into intimate contact with the "carbonaceous concrete," rapidly acts on its heat-resisting element, viz., the carbon. This corroding action continues until the slag recovers its healthy tone, and all practical men, I dare say, will agree that, until the hearth regains its original condition, inferior work is to be expected from the furnace.

Whether this explanation of the resistance of a furnace to the enormous strain upon its structure is the correct one or not, I feel very confident that Mons. Grüner would, after a careful examination of the working of the blast furnaces in the North of England, admit that the precipitated carbon cannot be burnt by the oxygen still remaining in the ore, and, on the contrary, that it arrives in great abundance in the hearth of the furnace. Again, whether it is the identical carbon which is found in the pig iron or not, will probably remain a subject of speculation, but I think I have given sufficient reason for regarding it as the probable source of the element.

SECTION XLV.—CONCLUSION.

My labours are now brought to a close, after greatly exceeding the limits within which I expected they would be confined, and unfortunately, perhaps, they terminate without comprehending all I wish they should have embraced.

The work, in which I have been engaged, instead of being issued after all my views were matured, made its appearance while the researches upon which they were founded were in progress, and as quickly as my other engagements would permit me to devote the necessary time to the classification of my experiments. This mode of procedure has its inconveniences, which, no doubt, will be detected by those who expect in the present to find a carefully compiled and condensed exposition of the process of iron smelting. In some few instances, a slight modification of previously entertained opinions may possibly be found, dictated by more recently acquired knowledge, and in others I have preferred a repetition of ideas, published some months before, in order to secure, if possible, a clearer statement of my meaning. I know my fellow-manufacturers will excuse any shortcoming, knowing, as they do, the circumstances under which the work itself has been written, and I must hope for equal indulgence at the hands of men of science who may feel interested in its contents, and who may value it, as recording the experience of one actively engaged in the process he has attempted to expound.

Without presuming too much upon any value of personal knowledge of a manufacture, gathered up during fully 25 years of study, I may be permitted to refer, with some degree of confidence, to the abundant opportunities I have enjoyed, obviously beyond the reach of any individual of purely scientific research, of gaining information from the most distinguished iron manufacturers and metallurgists of their day. Of the importance to which I myself attach to experience and assistance so obtained, sufficient evidence will be found in what I have written; but I cannot, without expressing my gratitude, take leave of those who have never withheld

any help I sought for at their hands, and which I have always endeavoured, in its proper place, to acknowledge in suitable terms.

This discharge of a duty to others would be incomplete, were I to omit making kindly mention of the assistance I have received at the hands of the manager of the Clarence Works, Mr. John Thompson. His accurate knowledge of the working of a blast furnace, acquired during a period of nearly 27 years in the service of my firm, enabled him to select the most appropriate periods for illustrating the phenomena I wished to explain, and the real interest he felt in my labours was a sufficient stimulus to induce him, upon many occasions, to bestow several consecutive hours in patiently watching and recording facts which find a place in these pages.

When I have had to examine opinions at variance with my own, I have studied to express my dissent in a manner so as to offend no one, feeling sure, at the same time, that the sole object of both sides was the honest pursuit of the truth. I will not enlarge upon the great benefit arising from personal intercourse among men engaged in the same pursuits and cultivating the same knowledge; but I may be allowed to express that which, I am sure, is the general feeling of my colleagues in the trade, that nothing, in our own time, has done more towards the useful interchange of thought among manufacturers of iron, than the establishment of the Iron and Steel Institute. For myself, personally, I cannot speak in too grateful terms of the opportunities it has been the means of affording me of extending my information in a question in which I feel so deep an interest.

Of the subject of my present labours, I have spoken as if we had reached, or almost reached, the bounds of perfection. In a sense, this may be so, but at the same time, we frequently fall far short of it, by an omission of some minor precautions connected with the proper preparation of our materials; and, in other instances, there is a disregard of those conditions, requiring only patient study to be appreciated, conditions, which cannot be neglected without entailing certain loss.

The near approach to perfection, however, to which I have alluded, is strictly confined to the production of our pig iron with a minimum quantity of materials, as we at present receive them.

I have, in Section XLI., endeavoured to lay down the grounds which impose a theoretical limit upon the reduction of fuel consumed in the manufacture of pig iron, and I have further attempted to define what I conceive this limit to be. This was founded upon a careful examination of the chemical properties of the agents employed in the smelting process, supplemented by many experiments and observations on the blast furnace itself. There exist, as I have explained, so many causes which interfere with the calculations made use of, that I feel it necessary to remark that it must not be understood that I draw a rigid line which cannot, under any circumstances, be departed from. More careful attention to the quality of our fuel, to the condition of our ironstone and flux, in the directions I have pointed out, may enable us possibly to effect *a little* further saving in the coke required in the operation. The rigid line in question, therefore, must not be considered as one which indicates within a few pounds the minimum of fuel, but it is one which is defined by the existence of physical laws, not sufficiently appreciated, I apprehend, by those who believe that larger capacity of the furnace, alteration in its form, or a greater intensity in the temperature of the blast, can effect savings rendered impossible by natural causes.

Whatever may be said in praise of the progress made in the smelting process itself during the last fifty years, all improvement may be said to be restricted to two objects, viz., increasing the make of a furnace, and decreasing the consumption of fuel. In one most important question, little, or no progress whatever has been made—that of improving the quality of the product. The ore goes in at the top, and, consistently with the furtherance of the two objects just mentioned, we receive at the bottom whatever the furnace chooses to give us, without a thought, generally speaking, being bestowed on the possibility of intercepting any of the impurities on the way; indeed, it is only within recent years that an ironmaster dreamt of connecting any inferiority in his make with the presence of any distinct impurity in the metal, iron from one ore being spoken of as if it were almost a distinct variety of one and the same substance.

It is true, the demands of commerce, hitherto, have given little encouragement towards incurring any great outlay in the suggested

direction. The very cheapness of iron has been the means of introducing its use in a thousand ways to which high price would have shut the door, and when a better article for higher class work was required, it was easier and less expensive to go at once to better class iron, than engage in costly experiments for the purpose of freeing the cheaper article of its imperfections.

Such was the state of things, a few years ago, when the cost of producing a ton of pig iron, free from phosporus, probably did not exceed by 10s. that of Cleveland, with its 1, or 1½ per cent. of this element.

The introduction of Bessemer steel for railway bars, the necessity of constructing our locomotives and iron steamers, of great strength, combined with great lightness, have changed all this. Steel is now a form in which iron will be greatly sought after, and in such anxious request is pig iron, suitable for the manufacture of this material, that it has run up rapidly from about 60s., to nearly £6 per ton; being nearly double that of pig iron obtained from Cleveland stone.

The limit to the production of Bessemer pig is the want of ores free from phosphorus. The hæmatites of this country, under the sudden demand, have doubled in price, and speculators, of all kinds, are rushing off to Spain, where tracts of land, conceded without any payment a few months ago by the government of that country, are said now to be worth large premiums; at least, such is the impression left on the mind by a perusal of the published prospectuses of the day.

This may be correct, and so firm may be the grip that phosphorus holds on iron that breaking up the bonds that bind them together may defy the skill of our most scientific men; but it may be well to remember that the yearly make of iron from Cleveland stone alone, contains about 30,000 tons of phosphorus, worth, for agricultural purposes, were it in manure as phosphoric acid, above a quarter of a million, and that the money value difference between Cleveland and hæmatite iron is not short of four millions sterling, chiefly due to the presence of this £250,000 worth of phosphorus.

The Pattinson process does not leave one part of silver in 100,000 of lead; the Bessemer converter robs iron of almost every contamination except phosphorus, but nine-tenths of this ingredient is

expelled by the puddling furnace. It may be difficult, but let it not be supposed there would be any surprise excited in the minds of chemists, if a simple and inexpensive process for separating iron and phosphorus were made known to-morrow, so that only one of the latter should be found in 5,000 of the former; and now that there is such a margin to stimulate exertion, we may be sure the minds of properly qualified persons will be directed towards the solution of a question of such national importance.

NOTE TO SECTION XIV.

The experiments detailed in Section XIV. show clearly that metallic iron can act on pure CO, forming some oxide of iron and setting free carbon, thus—

(A.) $$a\,Fe + b\,CO = Fe_a\,O_b + b\,C.$$

On the other hand, it has been shown in Section XI. that a mixture of oxide of iron lower than $Fe_2\,O_3$ and carbon furnishes by heat alone metallic iron, CO and CO_2, thus—

(B.) $$Fe_m\,O_{2n} + 2\,n\,C = m\,Fe + 2n\,CO.$$

(C.) $$Fe_m\,O_{2n} + n\,C = m\,Fe + n\,CO_2.$$

Again, it has been shown in Sections IV. and V. that $Fe_2\,O_3$ exposed to the action of CO, gives CO_2 and a lower oxide, thus—

(D.) $$p\,Fe_2\,O_3 + q\,CO = Fe_{2p}\,O_{3p-q} + q\,CO_2,$$

there being good grounds for supposing that 3 p-q is always a positive quantity (*i.e.*, q always is less than 3 p); or, in other words, that carbonic oxide *alone* is incapable of producing metallic iron, that office being performed by deposited carbon in accordance with equations (B) and (C) probably the lowest point to which CO *alone* can reduce $Fe_2\,O_3$ is expressed by the composition $Fe_2\,O$.

Experiments 331 to 337 show that, up to a bright red heat, the tendencies expressed by equation (A) predominate over the others, metallic Fe, under the influence of CO, at all temperatures up to, and including a bright red heat, becoming more or less oxidized and impregnated with carbon.

On the other hand, experiments 358 to 361 and 367 to 368, show that considerable quantities of carbon may be deposited without the formation of any metallic iron whatever, which may be considered due either to a hypothetical catalytic splitting up of CO into C and CO_2, thus—

(E.) $$2\,CO = C + CO_2,$$

(as mentioned on page 128); or to the power of a lower oxide of iron than $Fe_2\,O_3$, to act on CO in a manner similar to that expressed in equation (A), a higher oxide and free carbon being simultaneously produced, thus—

(F.) $$Fe_x\,O_y + z\,CO = Fe_x\,O_{y+z} + z\,C.$$

Inasmuch as there appears no ground for attributing the production of C and CO, to dissociation by heat alone, while equation (F) is, *à priori*, probable, the preference must be given to it, as a means of accounting for the first production of carbon by the action of CO on $Fe_2\,O_3$; this carbon then gives rise to the production of metallic iron as in equations (B) and (C); and, finally, this iron re-forms carbon by equation (A).

ERRATA.

Page 11.—Twenty-second line, for "840°C.," read "820°C."
,, 13.—Fourth and eighth lines, omit words, "a number of."
,, 16.—Twentieth line, for "412°C, 774°F," read "417°C. 782°F."
For "Co," read "CO," page 18, last line; page 23, 23rd and 24th lines; page 27, 16th line.
,, 26.—Twenty-second line, for "62·2," read "63·2."
,, 29.—Twenty-first line, after "per cent.," insert "of."
,, 35.—Thirteenth line, for "Exp. 143 maximum," read "Exp. 143 minimum."
,, 41.—Fifth line, after words, "altered capacity," insert "of the structure."
,, 43.—Second line, for "1,200°F.," read "1,200°C."
,, 45.—Sixteenth line, for "exists," read "exist." 26th line, after "influence," insert "texture and."
,, 49.—Thirtieth line, for "34 to 39," read "36 to 41."
,, 51.—Sixteenth line, for "receivi," read "receiving."
,, 52.—Twenty-sixth line, for "Fe O+CO+CO_2," read "$Fe_2 O_3$+CO+CO_2."
,, 52.—Exp. 236, for "200°C.," read "full red heat."
,, 53.—Thirty-sixth line, to "Exp.," add "239."
,, 54.—Twelfth line from foot, for "and," read "from."
,, 56.—Third line, for "160," read "229."
,, 56 and 57, in Expts., 247, 248, 249, 250, 251,
for ... 41·8 50·8 34·8 35·6 18·5
read ... 34·0 33·3 28·5 28·7 12·5
,, 58.—For "146 to 147," read "43 to 48."
,, 59.—"Exp. 270" ought to precede previous paragraph.
For "Co_2," read "CO_2," page 64, first line; page 81, fourth line.
Page 67.—Thirteenth line, for "$\frac{1}{2}$," read "$\frac{1}{4}$."
,, 68.—17th, 18th, 27th, 37th lines, and 1st line, page 69, instead of words, "per cent., or, per cent. of CO," read "CO_2 per 100 of CO."
,, 69.—Second line, after "22·3," insert "per 100 Fe."
,, 75.—Last line, for "336," read "332."
,, 77.—Last line, for "7," read "twelve." Page 78, third line, equation should be "25 CO+Fe=13 C+Fe O+12 CO_2."
,, 80.—For "of a portion," read "or a portion."
,, 85.—Fourteenth line, for "dull red heat," read "bright red heat."
,, 86.—First line, for "similar," read "The following."
,, 88.—For "quammes," read "grammes."
,, 95.—Fourteenth line, for "Co O_3," read "Co_2 O_3."

Page 101.—Under words, "Exps. 431 and 432," insert "oxide." Page 114, 26th line, for "loss heat," read "heat loss."

,, 117.—Twelfth line, for "27·7=27·7," read "29·7=29·7."

,, 125.—Exps. 461 *et seq.* for "CO lost by Ca CO_3," read "CO_2 lost by Ca CO_3."

,, 126.— ,, 470 for "Ca CO_4, read "Ca CO_5." Page 127, fifteenth line, for "to 760," read "and 760."

,, 136.—Eighth line, for "60 ft. and 76 ft.," read "50½ feet and 60 feet."

,, 146.—Thirteenth line, for "449," read "499."

In the conversion of the centigrade to Fahrenheit scale whole numbers are preserved. This may occasionally lead to differences, according as the reduction has been made from C. to F., or from F. to C. Besides these, one or two errors have been overlooked—

Page 7		12		17	31	37	45	55	57	58	62
for 268	1830	2190	1207	790	1180	268	1432	268	832	778	401
read 266	1832	2192	1202	770	1184	279	1472	266	842	770	410

Page		81			
for 452	470	472	472	420	452
read 440	489	464	464	430	440

Page 156.—After 17th line, insert the following table after words "smelting calcined Cleveland stone":—

	Composition of Gases by weight.			Carbon.	Oxygen.	Nitrogen.
Exp. 513.	CO_2 ...	11·80	= ...	3·22	... 8·58	
	CO ...	30·49	= ...	13·07	... 17·42	
	H ...	·11				
	N ...	57·60	...		...	... 57·60
		100·00		16·29	26·00	57·60

Page 164.—Sixteenth line, after "30,000," add "for Cleveland stone."

,, 167.—Sixteenth line, for "evolves heat by its union with the metal, and that this extra quantity is proportionate to the additional oxygen," read "evolves no heat by its union with the metal."

,, 179.—Sixth line, for "18·83" read "18·86 cwts."

,, 179.—At two lines from bottom, for "carbonic acid," read "carbonic oxide."

,, 187.—Seventeenth line, for "24" read "·24."

,, 193.—Twenty-first line, after "the two together," insert ("CO_2 and blast.")

,, 220.—Twelfth line, for "to," read "with."

,, 248.—Sixth line, for "2½ feet," read "21½ feet."

,, 256.—Twenty-fifth line, for "weeks," read "days."

,, 282.—Seventh line, for "2·738," read "2·758."

,, 289.—Twenty-third line, for "occasionally," read "sometimes."

,, 298.—Fourth line, for "considering," read "examining."

,, 336.—Ninth line, for "15,21," read "15·21." Twenty-fourth line, for "rising," read "raising."

,, 357.—Twenty-eighth line, for "its treatment," read "treating this mineral."

,, 365.—Fourteenth line, for "detoriorate," read "deteriorate."
,, 366.—Fifteenth line, for "consideration," read "examination."
,, 370.—Third line, for "pig iron," read "the pig iron."
,, 371.—Second line, after word "quantity," insert "by the use of heated air."
,, 373.—Sixth line, for "I maintain," read "as I maintain."
,, 375.—Sixth and eighth lines, for "Ca O_3," read "Ca CO_3."
,, 378.—Twenty-fifth line, for "19·04," read "19·08."
,, 379.—Second line from foot, for "20·58," read "20·62."
,, 394.—Eighth line, for "esser," read "lesser."
,, 415.—Twenty-third line, for "were," read "was."
,, 420.—Fifteenth line, for "meet," read "melt." 29th line, for "fully," read "about."

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